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A COMPARISON OF THE CHARACTERISTICS OF CERTAIN ION EXCHANGE RESINS

D. I. Ryabchikov, M. M. Senyavin and K. V. Filippova

(The V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R Academy of Sciences, Moscow)

Tsvet's chromatographic method [1] is widely used at the present time both in scientific research and in a number of branches of industry [2-4]. It is of particular importance in analytical chemistry [5-10]. We may mention, e.g. [8,9], the chromatographic separation of aluminum from zinc and iron, of arsenic from tin and antimony, the separation of metals in the presence of complex-forming compounds (separation of bismuth from copper and lead, and of tin from antimony), the determination of small amounts of sulfur, phosphorus and arsenic in nickel and copper. The determination of molybdenum in ferro-molybdenum with the help of sulfonated coal is of great interest [10]. The chromatographic determination of copper and iron in ceramic melts is of great importance.

Illustrative of the importance of the chromatographic method for analytical chemists is the extraordinary interest which the report read by V. N. Lenska on chromatography at the Conference on Classical Methods of Chemical Analysis[1] evoked.

The simplest problems of chromatographic analysis (e.g. the separation of components in the anionic form from a mixture of cations) can be solved in practice by means of any ion exchange material. But more complicated problems (e.g., separation of a mixture of cations which possess similar properties,etc.), can only be solved by the correct choice of all the experimental variables, particularly of the ion-exchange resin.

During the post-war years a number of institutes and enterprises in our country have achieved considerable success in the production of high-quality ion-exchange resins. Nevertheless as was demonstrated at the conference mentioned above, the overwhelming majority of analytical chemists are totally unacquainted with the brands of ion-exchange resins available and their characteristics. The present article is an attempt to fill the gap to some extent, and to acquaint a wide circle of analysts with the fundamental properties of cationites and anionites[2] at our disposal in comparison with foreign brands.

Synthetic resins used for ionic exchange purposes in their structure and

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1) The conference was held on the 14-17th of November, 1951, in Moscow.

2) In our work factory produced ion-exchange resins were used as well as those developed and prepared in the Mendeleev MKhTI. The authors wish to express their gratitude to I. P. Losev and A. B. Davankov for a gift of samples and for their close cooperation in the work. (MKhTI = Moscow Chem.-Tech. Inst.).

chemical composition are very similar to those synthetic resins used industrially as plastics, and are obtained in a similar fashion by condensation and polymerization [11]. According to our result on the elemental analysis of ion exchange resins of foreign manufacture the American cationite Amberlite IR-120 is prepared by polymerization, while the German Wofatit is a condensation product of phenol and formaldehyde. Preference should be given to polymerization ion exchange resins because of their greater chemical stability and because of the possibility of preparing unifunctional cationites by polymerization.

There are a number of requirements for resins used for the preparation of plastics and ion exchange purposes which are identical. Firstly a high mechanical stability, insolubility in water and the usual organic solvents, and low tendency to swell. Mechanical stability and insolubility can be attained by a high degree of condensation or polymerization and by the formation of a net-like three-dimensional structure for the polymer.

In the production of resins to be used as plastics, all technological processes are directed to making a chemically inactive product. In the production of ion exchange resins on the other hand it is endeavored to give them a more active character.

In accordance with their chemical nature all synthetic exchange resins used in practice for ion exchange can be divided into two groups. The first group comprises those resins which have acidic properties and can be used for the exchange of cations- cationites. While to the second group belong those resins which have basic properties and can be used for the exchange of anions - anionites. Cationites usually contain the active groups: $-SO_3H$; $-CH_2SO_3H$; $-COOH$, phenolic groups $-OH$, etc. The ion-exchange properties of anionites are determined by the presence of amine and imine groups.

The processes of exchange and regeneration of ion-exchange resins are described by the following reactions:

Cationite: $3RNa + FeCl_3 \rightleftharpoons R_3Fe + 3NaCl$ (exchange)
$RNa + HCl \rightleftharpoons RH + NaCl$ (regeneration)

Anionite: $2RCl + H_2SO_4 \rightleftharpoons R_2SO_4 + HCl$ (exchange)
$RCl + NaOH \rightleftharpoons ROH + NaCl$ (regeneration)

Before considering the characteristic properties of ion-exchange resins, which depend on their nature, we should like to point out the desirable features of ion-exchange resins from the point of view of chromatographic analysis.

In the production of ion-exchange resins, particles of both spherical forms and other forms not so desirable may be prepared. From the standpoint of chromatographic analysis there is no doubt that spherical particles are the most desirable, since they ensure close and even packing of the ion-exchange resin in a column, which in turn leads to a fuller use of the exchange capacity as a result of the favorable hydrodynamical conditions. The extent to which the ion-exchange resin will be used will also be greater the closer to equilibrium the operating conditions of the column.

The kinetics of the ion-exchange process in the overwhelming majority of cases is determined by the diffusion of the ions to the grain surfaces and inside them. The smaller the grain size, the faster is the equilibrium distribution of the ions between solution and the ion-exchange resin achieved, i.e. the faster the exchange process. In this connection the resistance of the layer is a limiting factor, which increases with decreasing grain size.

It is sometimes stated that a decrease in grain size leads to an increase in the static exchange capacity. This is incorrect, since ion-exchange resins have

a porous structure. As proof of the porosity of ion-exchange resins we quote the experimental results in Table 1 where it is shown that the static capacity of one of the Wofatit samples is independent of the grain size. It is obvious that the increase in the external surface as a result of grinding of the grains is practically negligible in comparison with the total surface of the porous ion-exchange resin.

Of the properties which depend on the nature of the ion-exchange resin, we have considered in the present article:, specific gravity, extent of swelling, static exchange capacity, and the potentiometric titration curves of the ion-exchange resins.

TABLE 1

Grain size in mm	Static exchange capacity in mg-equiv./g
<0.2	2.78
0.2 - 0.35	2.78
0.5 - 0.75	2.79
0.75 - 1.0	2.74
1.0 - 1.5	2.69

A knowledge of these fundamental characteristics will enable a rational choice to be made of ion-exchange resins for some of the actual problems which confront analytical chemists.

Before starting to test these samples they were all treated in accordance with the testing methods for ion-exchange resins for confirmation of their quality according to All-Union State Standard (5695-52).

Cationites were purified from mineral contaminants and converted into the hydrogen form by treating them with 2N HCl, followed by washing with distilled water till no reaction for chloride is given. Anionites were treated, first with 2 N HCl as for the cationites, and then for conversion into the hydroxyl form with 4% NaOH solution, followed by washing free from excess alkali with distilled water.

It should be noted that it is sometimes recommended that anionites may be converted into the hydroxyl form by treatment with 5% sodium bicarbonate (pH~8). If such a treatment is given, strongly basic anionites may be converted into the bicarbonate form, and as our experimental results show (see Fig.6) even weakly basic anionites are not completely converted into the hydroxyl form by the bicarbonate.

All tests were conducted with air-dried ion-exchange resins.

It is necessary to pay special attention to the removal of mineral contamination from ion-exchange resins. According to GOST[1] a solution of potassium thiocyanate may be used for checking the removal of mineral contaminants, since iron is the most likely contaminant as the result of the use of apparatus made of that metal for manufacturing the resins. In conducting an analysis of a definite mixture of elements it must be checked beforehand that these elements are absent in the resin to be used. In addition, it should be borne in mind that the resin might contain some of the original unreacted organic components, which might possess reducing properties. In some cases, where the chemical stability of the resin is insufficient, some of the organic material might be transferred into the filtrate.

The Physical Properties of Ion-Exchange Resins

According to GOST methods of testing ion-exchange resins, the following physical-mechanical properties are determined: moisture content, specific gravity (of the granular dry material, i.e. the apparent specific gravity), extent of swelling in water, mechanical stability, and granular composition.

The moisture content of an ion-exchange resin, which depends on the relative humidity of the air, is not of fundamental importance for the analytical applications of cationites or anionites, so that no figures on the moisture content are

1) GOST = All-Union State Standard.

given in the present paper. Mechanical stability, while important for industrial applications of ion-exchange resins, is of no interest for analytical chemists.

The granular composition of an ion-exchange resin produced industrially is not important in the application of ion-exchange resins for analytical purposes, since according to what has been said above very small grains should be chosen. Thus for technical purposes, grains of Espatite-1 whose diameter is less than 0.3 mm are regarded as waste products; at the same time fractions less than 0.1-0.2 mm are quite often used. In the present article therefore only results on the apparent specific gravity and the relative extent of swelling are given. These determinations were made according to GOST in measuring cylinders with samples of ca.10 g. Since ion-exchange resins are used in other solvents as well as water for analytical purposes, results for extent of swelling are given in water, N KCl, benzene and butyl alcohol.

The true specific gravity of an ion-exchange resin was determined as follows. A known weight of the resin was placed in a weighed pycnometer. The resin was covered with benzene and the pycnometer reweighed. The difference in weights gives the weight of benzene. The volume of benzene was determined from its specific gravity at the temperature of the experiment. From the difference in volume of the pycnometer and the benzene the volume of the resin was determined. By dividing the weight of ion-exchange resin by its volume the true specific gravity was determined.

It is natural that the degree of separation attained in a chromatographic experiment is greater, the greater the exchange capacity of the resin in the column. For a given static capacity of an unit weight of an ion-exchange resin, the exchange capacity of the resin in the column is greater, the greater the apparent specific gravity of the resin and the smaller its relative extent of swelling.

A knowledge of this latter quality is also of great importance, because the capacity of an ion-exchange resin (in the absence of complex forming compounds) is higher, the lower its extent of swelling, since in this case separation is connected with hydration of the ions [12]; in the case of a strongly swollen ion-exchange resin, ions of different degrees of hydration will be adsorbed by the resin to practically the same extent; on the other hand, in the case of a polymer with a stable structure only the non-hydrated ions will be sorbed, and differences in the energy of hydration will lead to a separation of the mixture being analyzed into its components.

Experimental results on the specific gravity and relative degree of swelling of the cationites examined are given in Table 2.

On the basis of these results the following conclusions can be drawn:

1. The degree of swelling depends essentially on the nature of the solvent. Maximum swelling occurs in non-polar solvents such as benzene. On the other hand the swelling in butyl alcohol is particularly high.

2. The ion-exchange resins SDV-1, SDV-2, KN, KM, Dowex-50 and Amberlite IR-120 swell less in N KCl than in water; Espatite-1, SBS, Amberlite IRC-50 and Wofatit P and C swell more in KCl than in water. Swelling of sulfonated coal in water and N KCl is the same. Naturally the increase in volume of an ion-exchange resin in a solution of KCl depends not only on the swelling in the medium but also on the partial conversion of the cationite into the potassium form.

3. For separating mixtures in the absence of complex-forming compounds the most suitable resin, according to it relative degree of swelling, is SBS.

TABLE 2

Designation	Relative degree of swelling, %				Specific gravity	
	Water	1N KCl	Benzene	Butyl alcohol	Apparent	True
Espatite-1	14	50	0	62	0.74	1.33
SBS.	0	14	8	34	0.57	1.29
SDV-1	190	119	-	-	0.65	-
SDV-2	135	70	-	-	0.50	-
KN	25	22	-	-	0.40	-
KM	108	85	-	-	0.48	-
Sulfonated coal .	33	33	-	-	0.67	-
Dowex-50	24	16	0	15	0.80	1.32
Amberlite IR-120 .	26	18	0	17	0.71	1.29
Amberlite IRC-50 .	36	62	4	62	0.70	1.31
Wofatit P	12	17	4	30	0.69	1.31
Wofatit C	12	41	4	40	0.83	1.35

4. The apparent specific gravity of the cationites lies within the range 0.40-0.83 g/cm^3. The low apparent specific gravities of SBS and KN are to some extent compensated by their relative degrees of swelling.

5. The true specific gravity is practically the same for all the cationites.

Results for the physical properties of anionites are given in Table 3.

TABLE 3

Designation	Relative degree of swelling, %			Specific gravity	
	Water	1N KCl	Benzene	Apparent	True
MN	40	25	-	0.63	-
TN	1	6	-	0.34	-
N-0.	23	29	-	0.25	-
MMG-1	24	23	0	0.80	1.433
N	21	18	5	0.52	1.410
VS	27	16	0	0.34	1.546
TM	12	15	4	0.80	1.492
Wofatit E	44	31	-	0.80	1.485
Wofatit M	26	25	5	0.76	1.447
Amberlite IR-4B .	41	33	0	0.64	1.276
Amberlite IRA-400.	41	31	6	0.68	1.194

From Table 3 it can be seen that the swelling of a given anionite in water and 1 N KCl is almost identical. In a non-polar solvent such as benzene, anionites show minimum swelling. Anionites can be divided into three groups according to their swelling capacity:

a) anionites with a small degree of swelling, up to 21% (TN, N, TM);

b) anionites with average degrees of swelling (MMG-1, VS, N-0, Wofatit M);

c) anionites with large degrees of swelling, 40% (MK, Wolfatit-E, Amberlites IR-4B and IRA-400).

The small apparent specific gravities of anionites N-0, VS and TN are worthy of note.

From the tables it can be seen that the true specific gravity is practically the same for all the anionites with the exception of Amberlite IR-4B and IRA-400 which are characterized by a comparatively small value for the true specific gravity. The true specific gravity of VS is relatively high while its apparent specific gravity is very small, which possibly testifies to the large porosity of this resin.

Exchange Properties

The most important characteristic of an ion-exchange material is its exchange capacity, which is determined by the number of functional groups containing ions which can be exchanged. The exchange capacity of a resin is usually characterized by the values of the Total Exchange Capacity (TEC), the Static Exchange Capacity (SEC), the Dynamic Capacity at the point where ions stream through (DEC), and the Dynamic Exchange Capacity at the point where the concentration in the layer reaches its initial value (IDEC).

Both the Total and Static Exchange Capacities are determined under static conditions. The essential difference between these two capacities is that the Total Exchange Capacity gives the exchange capacity for any exactly known pH value of the equilibrium solution, while the Static Exchange Capacity characterizes the capacity for unknown pH's, which depend on the nature of the ion-exchange resin and the exchange ion, and also on the amount of ion-exchange resin and the concentration of the solution. The uncertainty in the pH value of the equilibrium solution in the determination of the Static Exchange Capacity is the consequence of the fact that the concentration of the hydrogen ions is equivalent to the number of the adsorbing ion exchange cations or anions, i.e. its capacity for a given set of experimental conditions. When this fact is taken into consideration, it becomes comprehensible that the Static Exchange Capacity has a physical significance only when it is determined under conditions for which the pH of the original and equilibrium solutions do not differ too much from each other (in excess alkali or acid).

The value of the Dynamic Exchange Capacity up to the point at which ions pass through the column (DEC) is determined by both static and kinetic factors and accordingly depends essentially not only on the nature of the ion exchange resin but also on grain size, flow speed of the solution, etc. A knowledge of this value is important for the calculation of set ups for softening and demineralizing water, for decolorizing solutions, extraction of valuable materials from waste products, etc. and is of no less importance for chromatographic analysis. The value of IDEC is identical with one of the values of the Total Exchange Capacity for a corresponding acidity of the solution.

In accordance with the concepts postulated above, results are given for the Static Exchange Capacity of cationites and anionites (determined both in acid and alkalies). Curves which express the Total Exchange Capacity at different pH values of the equilibrium solution are also given [13-14].

The Static Exchange Capacity was determined for 0.1N NaOH (for cationites) and 0.1N HCl (for anionites) by keeping a known weight of the ion-exchange resin in an excess of the acid or alkaline solution and titrating the non-reacted reagent with phenol red as indicator after filtering off the resin. The Total Exchange Capacity was determined according to GOST by potentiometric titration. The respective results are given in Tables 4 and 5 and in Figs. 1-10.

From Table 4 it can be seen that SDV-1, Amberlite IR-120, Dowex-50 have a very high capacity; the capacity of the remaining cationites, which is determined by the sulfonate group, is not greater than 4 mg-equiv./g.

TABLE 4

Cationite	Static Exchange Capacity
Espatite-1	4.4
SBS	3.5
SDV-1	4.3
SDV-2	4.0
KN	2.8
KM	9.4
Sulfonated coal	3.6
Dowex-50	4.9
Amberlite IR-120	4.7
Amberlite IRC-50	9.2
Wofatit P	3.9
Wofatit C	6.4

TABLE 5

Anionite	Static Exchange Capacity
MN	4.1
TN	3.2
NO	3.9
MMG-1	4.2
N	4.4
VS	3.4
TM	4.0
Wofatit E	3.4
Wofatit M	3.2
Amberlite IR-4B	8.0
Amberlite IRA-400	1.6

Cationites containing carboxyl functional groups (KM, Amberlite IRC-50 and Wofatit C) have the greatest exchange capacity. The high capacity of carboxyl ion-exchange resins testifies to the fact that in the method used for their preparation it is possible to introduce several carboxyl groups into one benzene ring. As Ryabchikov showed [15-16], numerous carboxylic acids form stable complex compounds, e.g. with the rare earths; as a result of this the cationites mentioned above can exhibit a selective action in relation to a number of elements.

This comparatively high exchange capacity of carboxyl cationite, however, is only manifested in alkaline media. As a result of the high degree of dissociation of the sulfonic acid, its hydrogen ions can be substituted by metals even in very acid solution; since the carboxylic acids are comparatively weak, their exchange capacity in acid solution will be practically zero, as graphically shown by the potentiometric titration curves.

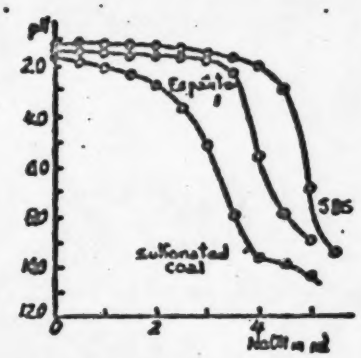

Fig. 1

From Table 5 it can be seen that the anionites MMG-1, N, TM and Amberlite IR-4B have a comparatively large capacity.

It is interesting to note that in contrast to cationites which contain sulfonate groups, the experimentally determined exchange capacity for anionites, with the exception of Amberlite IR-4B, is considerably lower than the capacity calculated from the percentage of nitrogen.

The potentiometric titration curves for cationites (Figs.1-4) can be divided into three groups according to their shape.

1) The curves derived by titration of the cationites SDV-1, SDV-2, SBS, Dowex-50 and Amberlite IR-120. These curves are similar to those of strong acids. Therefore it can be postulated that these brands of cationites contain only sulfonate groups on the benzene ring.

2) The titration curves of KN, KM, Amberlite IRC-50 and Wofatit C. These curves are similar to those for titration curves of comparatively weak acids. The step-wise character of the titration curves of KM and Amberlite IRC-50,

which is worthy of attention, is possibly explained by the presence of multibasic highly polymerized acids. The hypotheses that a few carboxyl groups enter into the benzene ring of the ion-exchange resin is confirmed by their very high Static Capacity (9.4, 9.2 mg-equiv/g).

3) Titration curves of Espatite-1, sulfonated coal, and Wofatit-P are intermediate between those of the first and second groups; on the one hand they have a fairly clearly defined horizontal part while on the other hand there is an even slope of the curve on addition of sufficient alkali. This may be explained by the presence of two types of acid groups in the cationites of the brands indicated (sulfonate and carboxyl or hydroxyl groups), or by the presence of sulfonate groups in the side chain.

For chromatographic analyses the most suitable cationites are those which possess maximum capacity at the pH of the solution being analyzed. It is appropriate to note that experiments can be carried out qualitatively only by bringing the ion-exchange resin into equilibrium with the washing solution beforehand. Values for the Total Exchange Capacity of the cationites for 3 pH values calculated from the potentiometric titration curves are given in Table 6.

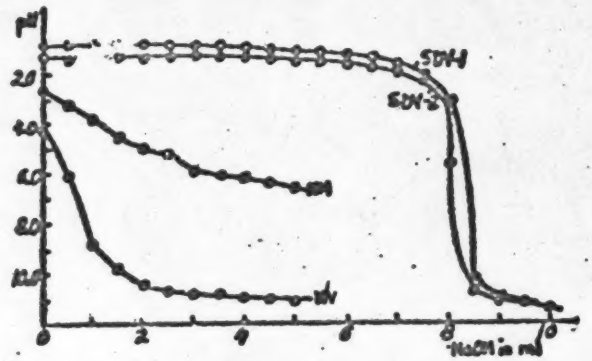

Fig. 2

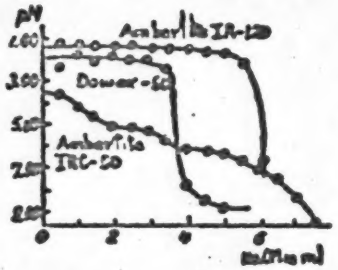

Fig. 3

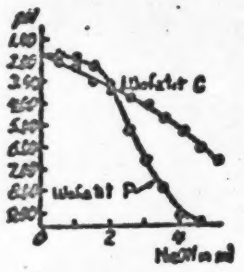

Fig. 4

Cationites the capacity of which does not depend on the acidity of the solution are sometimes called universal cationites.

The definite increase in capacity of a number of cationites on increasing the pH made it expedient to carry out experiments on less acid media. In chromatographic analysis in which complex-forming substances are used, this can be achieved by a corresponding decrease in the concentration of the complex-forming compounds. In view of the existing relation between the instability coefficients

of the complexes and the acidity of the solution, and its independence of the concentration of the components, the same relation between the normal and complex forms can exist in media of different acidities for a corresponding change in the concentration of complex-forming compounds.

TABLE 6

Cationite	pH		
	3	5	7
Espatite-1	1.9	2.0	2.1
SBS	2.25	2.4	2.5
SDV-1	4.0	4.2	4.3
KM	0.15	1.0	2.7
Sulfonated coals	1.0	1.5	1.7

On the basis of the potentiometric titrations of the anionites (Figs.5-10) the following conclusions can be drawn.

1) All the anionites tested can be divided into 2 groups (for a pH of 7).

2) Anionites of the first group can be used in neutral and even weakly alkaline media, while anionites belonging to the second and third group (weakly basic anionites) can only be used in acid media.

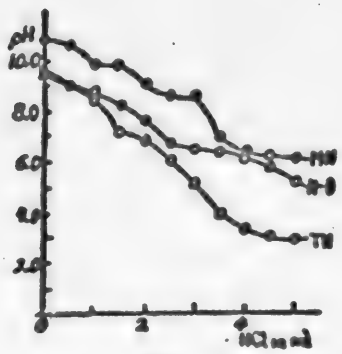

Fig. 5

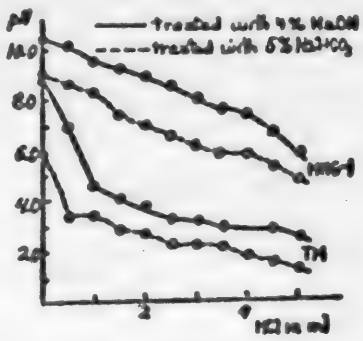

Fig. 6

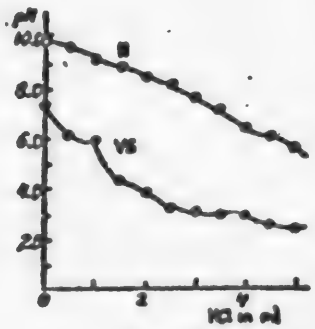

Fig. 7

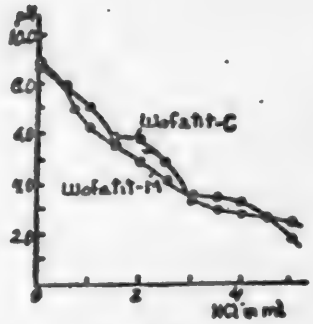

Fig. 8

3) From a comparison of the potentiometric titrations of anionites to convert them into the hydroxyl form with both 5% $NaHCO_3$ and 4% NaOH (see Fig.6) it is possible to conclude that even the weakly basic anionites are not completely converted into the hydroxyl form by means of 5% $NaHCO_3$.

4) From the shape of the potentiometric titration curves for VS, given a preliminary treatment with HCl (Fig.10), it can be postulated that this resin is amphoteric, i.e. possesses cationite properties as well. However this conclusion, based only on potentiometric titration, is not sufficiently reliable,

since curves of a similar type can be derived for anionites with weakly basic functional groups.

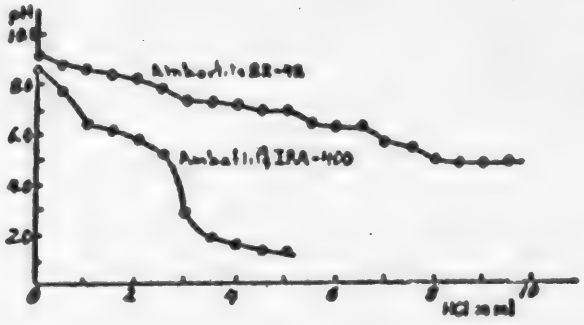

Fig. 9

Group I		Group II	
NO	1.25	TN	0.75
MMG-1	2.2	VS	0.2
N	1.75	TM	0.25
MN	1.75	Wo... t E	0.5
Amberlite IR-4B	2.15	Wo ... M	0.4
		Am... IRA-400	0.4

SUMMARY

1. Domestic cationites and anionites have been tested and compared with the best foreign ion-exchange resins from the point of view of their use in chemical analysis.

2. It has been shown that according to the apparent specific gravity and degree of swelling the most suitable domestic cationite and anionite respectively are SBS and MMG-1.

3. Judging by the total capacity within a wide pH range the most suitable cationites are SDV-1, SDV-2 and SBS. Of interest are those cationites with carboxyl functional groups (KM), which exhibit a selective action toward a number of elements.

Of the anionites tested, MMG-1 is recommended for analytical purposes

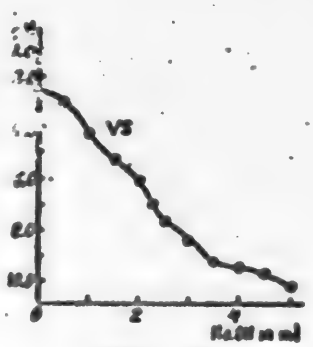

Fig. 10

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TITRATION OF MIXTURES OF TWO ACIDS OR THEIR SALTS

N. P. Komar

(A. M. Gorky Kharkov State Institute).

The titration of mixtures of two acids has been treated in an elementary form by Noyes [1] and his conclusions were used by Kolthoff [2]. A detailed examination of the question from the standpoint of potentiometric analysis was given by Roller [3]. In this paper the same question is considered from the viewpoint of ionic equilibrium, but individual problems are solved in a general form, and simplifications introduced only in the order of the analysis of the general solution.

Let us assume that to a mixture of two weak acids HA_1 and HA_2 there is added an amount of NaOH solution such that the initial concentrations of the three components are equal: $c_{HA_1} = c_1$ and $c_{HA_2} = c_2$ and $c_{NaOH} = c_1$ mols/liter. Such a system corresponds to the first stoichiometric point. If we assume that at the moment when all HA_1 is completely neutralized HA_2 is completely untouched, then the initial conditions can be represented by the following scheme:

$$c_{A_1^-} = c_1,\ c_{HA_2} = c_2,\ c_{Na^+} = c_1.$$

It is obvious that the equilibrium in this system will be determined by the equations:

$$HA_2 \rightleftarrows H^+ + A_2^-; \quad H^+ + A_1^- \rightleftarrows HA_1.$$

This system contains 5 unknowns: $[H^+] = x$; $[A_1^-] = y$; $[A_2^-] = z$; $[HA_1] = u$, $[HA_2] = t$ and $[Na^+] = c_1$, in which the formula in the square brackets both here and in the rest of this paper denote the equilibrium concentrations. It is obvious that for the calculation of the equilibrium the following equations can be used:

$$xy = k_1u;$$

$$xz = k_2t;$$

$$c_1 = y + u;$$

$$c_2 = z + t;$$

$$c_1 + x = y + z.$$

This system of equations can be easily transformed into a cubic equation in x:

$$x^3 + (c_1 + k_1 + k_2)x^2 + (k_1k_2 + k_2c_1 - k_2c_2)x - k_1k_2c_2 = 0. \qquad (1)$$

By means of this equation it is possible to calculate $[H^+]$ and pH for the first stoichiometric point, i.e., at the moment when an amount of NaOH has been added to the mixture of acids which is equivalent to the initial concentration HA_1.

Equation (1) reduces to the formulas of Noyes and Kolthoff when the following simplifications are introduced:

1) for $c_1 = c_2 = c$ the equation can be rewritten in the form

$$(x + c + k_1 + k_2)x^2 - k_1k_2(c - x) = 0;$$

2) for $x \ll c$

$$x = [H^+] = \sqrt{\frac{k_1k_2c}{c + k_1 + k_2}};$$

3) for $k_2 \ll k_1$ and c we get Noyes' formula, which Kolthoff regards as exact, while for $k_1 \ll c$ we get the simplified formula of Kolthoff. It is obvious that the first assumption is automatically satisfied during the titration of weak dibasic acids, but is inadmissible for theoretical investigations of the titration of mixtures of two weak acids, if the conditions $c_1 = c_2$ remain unfulfilled.

For an exact calculation of pH in those cases where the initial concentration of NaOH in the system satisfies the condition $c_1 < c_{NaOH} = c < c_1 + c_2$ it is possible to use the equation

$$x^3 + (c + k_1 + k_2)x^2 + [(c - c_1)k_1 + (c - c_2)k_2 + k_1k_2]x - \\ - k_1k_2[c_2 - (c - c_1)] = 0. \qquad (2)$$

It can be derived exactly the same as (1) and can be converted into the latter when $c = c_1$. If $x = [H^+] \ll c$ then Equation (2) transforms into the quadratic equation:

$$(c + k_1 + k_2)x_2 + [(c - c_1)k_1 + (c - c_2)k_2 + k_1k_2]x - k_1k_2[c_2 - (c - c_1)] = 0.$$

The solution of the quantitative determination of one weak acid HA_1 in the presence of another HA_2 is connected with the problem of the distribution of the alkali between two acids. If $c_{HA_1} = c_1$, $c_{HA_2} = c_2$, and the system contains $c_{NaOH} = c_1$, then it can always be postulated that αc_1 mol of NaOH has been used for the neutralization of HA_1 and yields αc_1 mols of A_1^- ions. Then, it follows that $(1 - \alpha)c_1$ mol. of NaOH has been used for neutralizing HA_2, which means that $(1 - \alpha)c_1$ mols of A_2^- ions should be formed. In such a case it is possible to regard the equilibrium concentration of the OH^- ions to be vanishingly small, since the system contains free acid. Under these conditions the equilibrium concentrations are expressed as follows:

$[A_1^-] = \alpha c_1$, $[HA_1] = c_1(1 - \alpha)$, $[A_2^-] = (1 - \alpha)\cdot c_1$, $[HA_2] = c_2 - (1 - \alpha)c_1$ and

$$[H^+] = h.$$

If, further $k_{HA_1} = k_1$ and $k_{HA_2} = k_2$, then obviously:

$$h\alpha c_1 = k_1c_1\ (1 - \alpha)$$

and

$$hc_1(1 - \alpha) = k_2[c_2 - (1 - \alpha)c_1].$$

After dividing one equation by the other and transposing we find that

$$\frac{k_1}{k_2} = \frac{\alpha}{(1 - \alpha)^2}\left[\frac{c_2}{c_1} - (1 - \alpha)\right]. \qquad (3)$$

This expression shows that the possibility of determining one weak acid in the presence of another depends not only on the ratio of their dissociation constants, as Kolthoff showed but also on the ratio of their initial concentrations. Formula (3) completely characterizes the possibility of titrating two weak acids in aqueous solution with a fixed degree of accuracy. If, for a given value of α and the expected ratio of the initial concentrations, c_2/c_1, the actual ratio of the constants is less than the limiting value, then the separate determination of the acids in aqueous solution is impossible. In similar cases the problem could be solved by the application of differential solvents [6,7].

Consideration of the distribution of alkali between two weak acids in a general way can also enable a number of important conclusions to be drawn. Let us take 1 liter of solution containing c_1 mols of HA_1 and c_2 mols of HA_2 and to it add v liters of a c-molar solution of NaOH. Let $k_{HA_1} = k_1$, $k_{HA_2} = k_2$, $k_1 > k_2$, and $c_1 < cv < c_1 + c_2$. In this case it can be accepted that $c_{HA_1} = \frac{c_1}{1 + v}$, $c_{HA_2} = \frac{c_2}{1 + v}$ and $c_{Na^+} = c_{OH} = \frac{cv}{1 + v}$. Assume that for the neutralization

of HA_1 an α part of the NaOH was used, then applying the above considerations we get the equations:

$$\frac{h\alpha cv}{1+v} = \frac{k_1(c_1 - \alpha cv)}{1+v} \tag{4}$$

and

$$\frac{h(1-\alpha)cv}{1+v} = \frac{k_2[c_2 - (1-\alpha)cv]}{1+v} \tag{5}$$

The product cv, which enters both equations, is equal to the number of mols of NaOH which was added to 1 liter of the mixture, containing c_1 mols of acid HA_1 and c_2 mols of acid HA_2 in order to get a pH corresponding to $[H^+] = h$, which enter into Equations (4) and (5). Let cv be denoted by z, then solving the system with respect to z and α, we get:

$$\alpha = \frac{c_1k_1(h+k_2)}{c_1k_1(h+k_2) + k_2c_2(h+k_1)} \tag{6}$$

and

$$z = cv = \frac{k_2}{h+k_2}c_2 + \frac{k_1}{h+k_1}c_1. \tag{7}$$

With the help of Formula (6) it is possible to calculate the distribution of alkali between the two weak acids, if $c_1 < cv < c_1 + c_2$. Formula (7) is far more important. It shows that the number of mols of NaOH expended on attaining any given pH lies between the first and second stoichiometric points and is a linear function of the initial concentrations of the weak acids c_1 and c_2. But if this is so, then by titrating the same mixture to different pH values and noting the respective values of h_i and z_i where i is the number of the respective value, it is possible to find the required values of c_1 and c_2, i.e., to determine the required concentrations of both the weak acids.

Finally, using Formula (6) it is possible to find in a general form the indicator error of the titration. It is obvious that this error is equal to $cv - c_1$, if $c_{HA_1} = c_1$ and if the titration is interrupted when the hydrogen ion concentration H^+ attains the value h. After substitution and simplification we find that the absolute indicator error will be equal to

$$cv - c_1 = z - c_1 = \frac{c_2k_2}{h+k_2} - \frac{hc_1}{h+k_1}, \tag{8}$$

and the relative error given by

$$\frac{z - c_1}{c_1} \cdot 100 = \frac{k_2}{h+k_2} \cdot \frac{c_2}{c_1} - \frac{h}{h+k_1} \cdot 100, \tag{9}$$

when it is obvious that the error will be zero if

$$\frac{k_2}{h+k_2} \cdot \frac{c_2}{c_1} = \frac{h}{h+k_1}.$$

Titration by the displacement method, which is based on the reaction between the salt of a weak acid and a strong acid, is usually considered in isolation from the medium in which it is performed. We adopt such an approach, however, only in the case where the solution of the salt is prepared and kept under conditions which exclude CO_2 absorption from the air.

If it is accepted that the solubility of CO_2 in water at room temperature is of the order of $3.8 \cdot 10^{-2}$ mol/liter, then at a concentration of CO_2 in the laboratory air of the order of 0.05 vol.%, it is possible to assume that the equilibrium concentration of CO_2 in any aqueous solution open to the air will be roughly $2 \cdot 10^{-3}$ mol/liter.

Under such conditions a solution of a salt NaA, for which $c_{NaA} = c_{Na^+} = c_{A^-} = c$ represents a complex system described by the equations

$$A^- + H^+ \rightleftarrows HA;$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-;$$

$$H^+ + OH^- \rightleftarrows H_2O.$$

In this system there are 5 unknowns: $[H^+] = x$, $[A^-] = y$, $[HA] = z$, $[HCO_3^-] = u$, $[OH^-] = t$.

Assume that $[H_2CO_3] = a = 2 \cdot 10^{-5}$ mol/liter, $k_{HA} = k$, $k_{H_2CO_3} = k_1 = 3.5 \cdot 10^{-7}$ and $k_{H_2O} = w = 10^{-14}$.

Applying the law of mass action to our three equations, and using the value of the initial concentration of the salt $c_{NaA} = c$, and the principle of the electroneutrality of the solution, we get the following system of equations:

$$xy = kz;$$

$$xu = k_1 a;$$

$$xt = w;$$

$$c = y + z$$

$$c + x = y + u + t.$$

This system reduces to an equation of the third order

$$x^3 + (c + k)x^2 - (ak_1 + w)x - k(ak_1 + w) = 0. \qquad (10)$$

In so far as the hydrogen ion concentration $[H^+]$ in not very dilute aqueous solutions of a salt of a weak acid is very small as compared to the initial concentration of the salt, i.e. $x \ll c$, Equation (10) is transformed into a quadratic

$$(c + k)x^2 - (ak_1 + w)x - k(ak_1 + w) = 0. \qquad (11)$$

With the help of this equation it is possible to calculate the actual pH of a solution of a salt NaA, in equilibrium with air and thence to calculate $[HCO_3^-] = \frac{ak_1}{x}$ and the total concentration of carbonate equal to $\frac{ak_1}{x} + 2 \cdot 10^{-5}$ mol/liter.

Results calculated by this method for 0.1 N solutions of salts of the type NaA of weak acids of different strengths are given in the following table.

TABLE

pH Values and Equilibrium Concentrations of Components in Equilibrium in 0.1 N Solutions of Salts of Weak Acids of the Type NaA, in Contact with Air Containing 0.05 vol.% CO_2

K_{HA}	$[H^+]$	$[A^-]$	$[HA]$	$[HCO_3^-]$	pH, Calculated	
					CO_2 accounted	From hydrolysis of NaA
10^{-5}	$2.6 \cdot 10^{-8}$	$9.97 \cdot 10^{-2}$	$3.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	7.6	8.0
10^{-6}	$8.4 \cdot 10^{-9}$	$9.92 \cdot 10^{-2}$	$8.0 \cdot 10^{-4}$	$8.0 \cdot 10^{-4}$	8.1	9.5
10^{-7}	$2.6 \cdot 10^{-9}$	$9.75 \cdot 10^{-2}$	$2.5 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	8.6	10.0
10^{-8}	$8.7 \cdot 10^{-10}$	$9.20 \cdot 10^{-2}$	$8.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	9.1	10.5
10^{-9}	$3.0 \cdot 10^{-10}$	$7.70 \cdot 10^{-2}$	$2.3 \cdot 10^{-2}$	$2.3 \cdot 10^{-2}$	9.5	11.0
10^{-10}	$1.2 \cdot 10^{-10}$	$4.55 \cdot 10^{-2}$	$5.45 \cdot 10^{-2}$	$5.45 \cdot 10^{-2}$	9.9	11.5

The results given in the table are of importance for the calculation of the amount of carbonates contained in solutions of salts of weak acids both during titration and also for making up buffer solutions.

These results also show that titration by the displacement method is practically always a titration of a complex mixture of two salts NaA and $NaHCO_3$ and acids HA and HCO_3^-. Therefore the theory of titration by the displacement method for one salt is only of significance in special cases.

The titration of a mixture of two salts of weak acids with a solution of strong acid is solved by the same method as that used for investigating the titration of a mixture of two weak acids with an alkali solution. Let $c_{NaA_1} = c_{A_1^-} = c_1$; $c_{NaA_2} = c_{A_2^-} = c_2$; $c_{Na^+} = c_1 + c_2$. At the first stoichiometric point $c_{HA_0} = c_{H^+} = c_{A_0} = c_2$, and at the beginning it can be assumed that $c_{Na^+} = [Na^+] = c_1 + c_2$; $c_{A_1^-} = c_1$; $c_{A_0^-} = [A_0^-] = c_2$ and $c_{HA_2} = c_2$. If the ionic strength of the solution is not taken into account, then it can be assumed that Na^+ and A_0^- ions will not affect the equilibrium. In this case the equilibrium is described by the following equations:

$$HA_2 \rightleftarrows H^+ + A_2^-;$$

$$H^+ + A_1^- \rightleftarrows HA_1;$$

$$H_2O \rightleftarrows H^+ + OH^-$$

and contains 6 unknowns: $[H^+] = x$, $[OH^-] = y$, $[A_1^-] = z$, $[HA_1] = u$, $[A_2^-] = v$, $[HA_2] = t$.

By arranging the system of equations as done previously above and solving it with respect to x, we get an equation of the 4th order.

$$x^4 + (c_1 + k_1 + k_2)x_3 + (c_1k_2 + k_1k_2 - c_2k_2 - w)x^2 - (c_2k_1k_2 + k_1w + k_2w)x - \\ - k_1k_2w = 0,$$

which can be used for exact calculation of pH. In determinations of this type c_1 and c_2 should never be less than 0.01 mol/liter. Under these conditions $c_1 \gg x$, k_1, k_2 and our equation can be reduced to the form:

$$x^3 + \frac{k_2(c_1 - c_2) + k_1k_2 - w}{c_1}x^2 - \frac{c_2k_1k_2 + w(k_1 + k_2)}{c_1}x - \frac{k_1k_2w}{c_1} = 0.$$

In these equations the index 1 refers to the stronger acid and the index 2 to the weaker acid. In this case $k_2 < k_1$ and the first stoichiometric point corresponds to the point at which the mixture contains an amount of NaOH equivalent to the initial concentration of the NaA_2.

For the case where c_{HA_0} in the mixture is equal to c, while $c_2 < c < c_1 + c_2$, it is easy to derive the equation:

$$x^4 + (c_1 + c_2 - c + k_1 + k_2)x^3 + [(c_2 - c)k_1 + (c_1 - c)k_2 + k_1k_2 - w]x^2 - \\ - (ck_1k_2 + k_1w + k_2w)x - k_1k_2w = 0. \qquad (12)$$

Where $x = [H^+] \ll c_1, c_2, c$, this equation assumes the form:

$$x^3 + \frac{[(c_2 - c)k_1 + (c_1 - c)k_2 + k_1k_2 - w]}{c_1 + c_2 - c + k_1 + k_2}x^2 - \frac{ck_1k_2 + (k_1 + k_2)w}{c_1 + c_2 - c + k_1 + k_2}x - \\ - \frac{k_1k_2w}{c_1 + c_2 - c + k_1 + k_2} = 0.$$

The distribution of H^+ ions between the anions A_1^- and A_2^- is solved just as above for the titration of a mixture of two weak acids with alkali. The question of the possible determination of NaA_2 in the presence of NaA_1 is solved by means of the formula:

$$\frac{k_1}{k_2} = \frac{\alpha}{(1-\alpha)^2}\left[\frac{c_1}{c_2} - (1-\alpha)\right],$$

which is derived in the same way as Formula (3) and differs from it only by the ratio $\frac{c_1}{c_2}$.

The solution of the distribution of $z = cv$ mols of acid, added to 1 liter of a mixture containing c_1 mols of NaA_1 and c_2 mols of NaA_2 is achieved by the method given above for the titration of two acids with alkali. From these results it seems that the distribution coefficient

$$\alpha = \frac{hc_2(h + k_1)}{hc_1(h + k_2) + hc_2(h + k_1)}, \qquad (13)$$

but

$$z = cv = \frac{h}{h + k_1} c_1 + \frac{h}{h + k_2} c_2. \qquad (14)$$

The indicator error in this case, as can be seen is equal to

$$\frac{z - c_2}{c_2} \cdot 100 = \left\{\left[\frac{h}{h + k_1} \cdot \frac{c_1}{c_2} - \frac{k_2}{h + k_2}\right]\right\} \cdot 100. \qquad (15)$$

In this case the value of cv is also a linear function of the initial concentrations of the salts c_1 and c_2. Titration to a fixed pH in which cv is taken into account, in this case also ensures the possibility of giving an approximate determination of the composition of a mixture of two salts of weak acids.

SUMMARY

1. General formulas are given for the calculation of the distribution coefficients of alkali between two weak acids or of H^+ ions between the anions of two acids.

2. It has been shown that the amount of strong alkali in the first case and of strong acid in the second case is a linear function of the initial concentrations of the weak acids or their salts.

3. A general method is given for the calculation of equilibrium for a solution of a salt of a weak acid in contact with air containing CO_2. Results are given of such calculations for 0.1 M solutions of salts of weak acids.

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AMPEROMETRIC TITRATION OF NICKEL WITH DIOXIMES

V. M. Peshkova and Z. A. Gallai

(M. V. Lomonosov Moscow State University)

Organic reagents which enable determinations of individual elements to be made without preliminary separation from other elements present are of great importance in amperometric titration methods. The shape of the titration curve depends on the nature of a given reagent. If the substance to be determined and the reagent give a diffusion current on applying an EMF to both, then the curve obtained will be V-shaped and will enable the equivalence point to be determined with great accuracy. Curves of this type are obtained when dimethylglyoxime, α-benzoinoxime, salicylaldoxime and a number of other reagents are used. In those cases where the reagent does not give a diffusion current on applying an EMF, the titration curves will be of the L form, which is less suitable for the determination of the equivalence point. Up to the present time a considerable amount of work has been done on the application of individual organic reagents in amperometric titration. Zanko [1], Stock [2], Stone and Furman [3] showed the possibility of using oximes for the determination of Mg, Zn, Cu, Al and Cd. The work of I. Kolthof [4] and Mukhina [5] on the use of dimethylglyoxime for the determination of Ni is also known. A number of organic reagents have been suggested for the determination of Cu: α-benzoinoxime (A. Langer [6]), α-nitroso-β-naphthol (I. Kolthof and Langer [7]), salicylaldoxime (A. Neuberger [8]), and quinaldinic acid (Stock [9]).

In the present paper, results are given for the use of dimethylglyoxime and its sodium salt and of the dioxime of cyclohexandioxime. The latter has been shown previously to possess a number of advantages over dimethylglyoxime. The work was carried out by means of a dropping mercury electrode. The concentrations of the Ni and dioxime solutions respectively were determined gravimetrically. $NiSO_4$ was determined by precipitation with dimethylglyoxime and the dioxime by precipitation with Ni salts.

The Use of Dimethylglyoxime and Its Sodium Salt

Determination of Nickel in Solutions of Its Pure Salts. Dimethyl glyoxime as a reagent for Ni was proposed by Chugaev [12], and has been widely used in analytical chemistry, both for the gravimetric and colorimeetric determination of Ni [13]. Some authors use the Na salt of dimethylglyoxime.

An essential condition in performing amperometric titration is the choice of the correct base solution. In this case we considered that the chosen electrolyte could be used for complex formation with Fe and Al. Sodium acetate and tartrate respectively, and sodium and ammonium citrates were considered. The half-wave potential of Ni is −1.1 V. After a number of preliminary experiments, it was established that it is best to titrate Ni in a base solution of 0.1 N Na-acetate for which a clearly defined diffusion wave was obtained. Polarograms obtained for Ni in NH_4-citrate and Na-tartrate did not have a clearly defined form and gave very small wave heights.

Dimethylglyoxime is reduced on the droping mercury electrode as shown by Kolthof [4] and Stromberg [15]. The polarograms were drawn visually and the

EMF checked with a Weston cell; gelatin was used as a maximum suppressor. With a base electrolyte of 0.1 N Na-acetate for a concentration of dimethylglyoxime of 0.002 M, the reduction potential E = -1.13 V and the half-wave potential $E_{1/2}$ = -1.40 V; while for 1 N NH_4OH and 0.1 N NH_4Cl the reduction potential E = = -1.14 V (see Curve 1 in the diagram).

A more clearly defined curve for amperometric titration was obtained when the EMF across the electrolytic cell was increased to a potential greater than the half-wave potential of the element being determined. We used a potential of -1.70 V.

Titrations were invariably carried out in open vessels without removal of oxygen from the solution. The results for titration of pure Ni solutions in a base electrolyte of 0.01 N Na-acetate are given in Table 1.

TABLE 1

Expt. No.	Ni taken in mg	Vol in ml	Ni found in mg	Error in mg
1	0.12	10	0.21	+0.09
2	0.30	10	0.31	+0.01
3	0.60	10	0.63	+0.03
4	1.20	20	1.23	+0.03
5	2.40	20	2.38	-0.02
6	3.60	20	3.57	-0.03

The volume of the titration solution is changed according to the Ni content. In the more dilute solutions the precipitate separates slowly, presumably because of the formation of supersaturated solutions; it is therefore necessary that titrations should be performed with amounts of Ni which are not less than 0.2-0.3 mg in 10 ml.

Determination of Nickel in the Presence of Other Elements. Ni was determined in the presence of Fe, Cr, and Al. It was established that for small amounts of Fe (Ni:Fe = 1:3), titration can be carried out satisfactorily with a base electrolyte of 0.1 N Na-acetate.

With increasing concentration of Fe it becomes necessary to use 2 N Na-acetate, while for even greater amounts of Fe, more than 1:10, it is recommended that the excess Fe should be first removed, preferably in the form of the double salt with NaF [14]. For large concentrations of Fe it is best to take a volume of 40 ml and to increase the concentration of the Na-acetate.

In the titration of mixtures of Ni and Al and of Ni and Cr, exactly the same pattern is observed. For small amounts of Al and Cr the titration is satisfactory when 0.1 N Na-acetate is used as the base electrolyte, but with increasing amounts of Al or Cr to ratios of 1:10 it is recommended that 2 N Na-acetate be used as with Fe.

TABLE 2

Expt. No.	Ni taken in mg	Ni:Fe	Base electrolyte	Vol in ml	Ni found in mg	Error in mg
1	1.20	-	0.1 N sodium acetate	20	1.22	+0.02
2	1.20	1:1	Ditto	20	1.23	+0.03
3	1.20	1:2	"	20	1.22	+0.02
4	1.20	1:3	"	20	1.23	+0.03
5	1.20	1:5	"	20	1.28	+0.08
6	1.20	1:8	2 N sodium acetate	20	1.23	+0.03
7	2.40	1:8	Ditto	40	2.42	+0.02
8	-	1:10	"	40	2.38	-0.02

In the determination of Ni in the presence of considerable amounts of Al and Cr (for ratios of Ni:Cr and Ni:Al = 1:10) equilibrium is only slowly attained after addition of each portion of the reagent.

Titration with a Solution of Sodium-Dimethylglyoxime. The reduction potential of Na-dimethylglyoxime with a base electrolyte of 0.1 N Na-acetate is the same as for dimethylglyoxime itself (see Curve 2 on the diagram). An aqueous solution of Na-dimethylglycxime was used. A characteristic of this reagent is the rapidity with which Ni can be determined because of the fast rate at which a state of equilibrium is reached during titration.

Titration can be carried out in the presence of Na-acetate and other electrolytes- 0.1 N NaCl and 0.1 N Na_2SO_4. Results are given in Table 3.

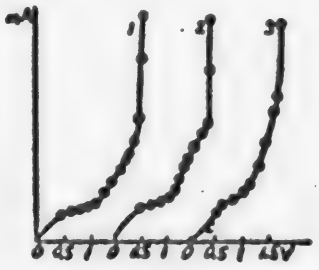
TABLE 3

Expt. No.	Ni taken in mg	Base electrolyte	Ni found in mg	Error in mg
1	1.20	0.1 N CH_3CO_2Na	1.21	+0.01
2	2.40	Ditto	2.43	+0.03
3	2.40	0.1 N NaCl	2.41	+0.01
4	2.40	0.1 N Na_2SO_4	2.42	+0.02

On the basis of these results it can be stated that Na-dimethylglyoxime can be substituted for dimethylglyoxime itself.

The Use of Cyclohexanedione-dioxime

Cyclohexanedione-dioxime has been tested as a reagent for Ni both by Peshkova, Gontaeva and Vedernikova [10] and by Johnson and Simmons [11]. Ni-cyclohexanedione-dioxime has a bright red color and is more stable in acid media (pH 3.3) than Ni-dimethylglyoxime. It is also considerably more stable in ammoniacal solutions. These important properties of Ni-cyclohexanedione-dioxime indicate that it will be useful for the determination of Ni in the presence of other metals. A 0.025 M aqueous solution of the reagent was used. It was estimated gravimetrically under conditions established previously.[1)]



The polarograms obtained with this reagent in a base electrolyte of 0.1 N Na-acetate show that its reduction potential E = −1.14 V and its half wave potential $E_{1/2}$ = −1.40 V, as for dimethylglyoxime (see curve 3 in the diagram). From experiments on the determination of Ni with cyclohexanedione-dioxime in solutions of pure Ni salts in the presence of different electrolytes, it was shown that a solution of Na-acetate or of the sulfate of an alkali metal in the presence of ammonia could be used as base electrolytes. From Table 4 it can be seen that the determination of Ni with this reagent can be carried out with an ammoniacal complex, which distinguishes it from dimethylglyoxime.

Titration of Nickel in the Presence of Zinc. The possibility of determining Ni with cyclohexanedione-dioxime in ammoniacal solution is of particular interest for the use of this reagent in the titration of Ni in the presence of Zn, since the

1) The reagent was made in Prof. A. P. Terentev's laboratory (Moscow State University) by A. I. Guseva by a method developed at the Institute for Chemical Reagents).

TABLE 4

Expt. No.	Ni taken in mg	Base Electrolyte	Vol., in ml	Ni found in mg	Error in mg
1	0.77	0.1N CH_3CO_2Na	10	0.77	0
2	1.55	Ditto	20	1.55	0
3	1.55	0.1N K_2SO_4 + 1 ml 10% NH_4OH	20	1.55	0
4	1.55	0.1N K_2SO_4 + 5 ml 10% NH_4OH	20	1.58	+0.03

latter combines to form an ammoniacal complex and does not interfere with the determination of Ni.

Under these conditions a clearly defined curve is obtained which gives reproducible equivalence points.

The results in Table 5 show that an excess of 1 ml NH_3 is sufficient. 0.1 N Na-acetate was used as the base electrolyte.

TABLE 5

Amount of Ni 1.55 mg, vol. 20 ml, NH_4OH 10%

Expt. No.	Ni:Zn	Base Electrolyte	Ni found in mg	Error in mg
1	-	0.1N CH_3CO_2Na	1.55	0
2	1:5	0.1N CH_3CO_2Na + 1 ml NH_4OH	1.50	−0.05
3	1:5	0.1N CH_3CO_2Na + 5 ml NH_4OH	1.57	+0.02
4	1:7	Ditto	1.53	−0.02
5	1:10	"	1.55	0.00
6	1:15	"	1.63	+0.08
7	1:15	0.1N CH_3CO_2Na + 7 ml NH_4OH	1.55	0.00
8	1:20	0.1N CH_3CO_2Na + 10 ml NH_4OH	1.57	+0.02
9	1:50	0.1N CH_3CO_2Na + 12 ml NH_4OH	1.54	−0.01

Titration of Nickel with Cyclohexanedione-Dioxime in the Presence of Aluminum and Iron. After a number of preliminary experiments it was established that in the presence of Al, Ni can be titrated with sufficient accuracy if Na-tartrate with added ammonia was used as the base electrolyte. Under these conditions Al and Ni are in the form of complex compounds.

In contrast to titration of Ni with dimethylglyoxime with Na-tartrate with added ammonia as base electrolytes, titration with cyclohexanedione-dioxime proceeds without any complications because the precipitate separates rapidly.

The obvious reason is the smaller solubility of Ni-cyclohexanedione-dioxime as compared with Ni-dimethylglyoxime.

Satisfactory results were obtained for ratios of Ni:Al from 1:1 to 1:70.

Favorable results for the determination of Ni in the presence of Fe were obtained with either Na-acetate or Na-citrate as base electrolytes, ammonia being added in both cases. Results are given in Table 7.

Complete satisfactory results were obtained for ratios of Ni:Fe of 1:60; results in Table 7 show that, at ratios of Ni:Fe = 1:20 and over that, Fe probably

TABLE 6

Amount of Ni 1.55 mg, vol. 20 ml, base electrolyte in all the experiments 4 ml saturated sodium acetate $Na_2C_4H_4O_6$ + 4 ml of 10% NH_4OH

Expt. No.	Ni:Al	Ni found in mg	Error in mg
1	1:12	1.53	−0.02
2	1:20	1.55	0.00
3	1:30	1.53	−0.02
4	1:50	1.54	−0.01
5	1:70	1.58	+0.03

forms a stable complex compound with Na-citrate. All these results show that cyclohexanedione-dioxime has definite advantages over dimethylglyoxime, in that it gives a compound with Ni which is characterized by a greater stability in ammoniacal media, which enables Ni to be determined in the presence of large amounts of Fe and Al, and enables Ni to be determined in the presence of Zn as well.

Use of α-Furildioxime

α-Furildioxime was investigated by V. M. Peshkova for use in the gravimetric and colorimetric determination of Ni. In the present work a 0.012 M alcoholic solution of this reagent was used. α-Furildioxime gives a reddish-terracotta colored precipitate with Ni. The reduction potential of the reagent in a base electrolyte of 0.1 N Na-acetate was found to be E = −1.14 V and its half wave potential $E_{1/2}$ = −1.40 V.

This reagent is not suitable for the amperometric titration of Ni since the precipitate does not form readily and only slowly coagulates at room temperature.

TABLE 7

Amount of Ni 1.05 mg, vol. 20 ml, NH_4OH 10%

Expt. No.	Ni:Fe	Base Electrolyte	Ni found in mg	Error in mg
1	1:4	0.1N CH_3CO_2Na + 1 ml NH_4OH	1.55	0.00
2	1:10	1N CH_3CO_2Na + 1 ml NH_4OH	1.56	+0.01
3	1:20	2N CH_3CO_2Na + 1 ml NH_4OH	1.51	−0.04
4	1:20	4 ml saturated sodium citrate + 1 ml NH_4OH	1.55	0.00
5	1:40	Ditto	1.56	+0.01
6	1:60	"	1.60	+0.05

TABLE 8

Alloy used	Elemental composition, %					Ni determined amperometrically
	Ni	Fe	Cr	Al	Mn	
Chromenickel steel	8.33	73.70	18.00	–	–	8.30 8.24
Manganesenickel alloy	76.50	–	–	2.00	23.50	76.20
Nickelaluminum alloy	98.00	–	–	–	–	98.70
Nichrome	60.00	20.0	20.0	–	–	60.08 60.02
Electroresistance steel	10.00	77.0	13.0	–	–	9.93 10.02

The results obtained by the methods described above were checked by analyses of several samples of Ni alloys of known composition.

Results given in Table 8 show that Ni can be determined by amperometric titration fairly accurately in alloys containing up to 60% Ni.

SUMMARY

1. Dimethylglyoxime, Na-dimethylglyoxime and cyclohexanedione-dioxime can be used for the amperometric titration of Ni in pure Ni salts and in the presence of Fe^{3+}, Al^{3+}, Cr^{3+} and Zn^{2+}.

2. For titration with dimethylglyoxime, Na-acetate is recommended as the base electrolyte.

3. Titration can be carried out at room temperature without the necessity of excludion of oxygen from the solution.

4. Cyclohexanedione-dioxime is preferred to dimethylglyoxime and Na-dimethylglyoxime because it can be used for the determination of Ni in the presence of large amounts of Al, Fe, Cr and Zn^{2+}.

5. It has been confirmed by amperometric titration that Ni-cyclohexanedione-dioxime is more stable than Ni-dimethylglyoxime.

6. It has been established that the dioximes tested are reduced at the same potential; the half wave potential $E_{1/2} = -1.40$ V.

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THE CONDUCTOMETRIC TITRATION OF ZINC WITH BARIUM HYDROXIDE

V. V. Udovenko and G. B. Pasovskaya

Central Asian State University, Tashkent

The conductometric titration of Zn with $Ba(OH)_2$ has been described by Kolthof [1]. Kolthof showed that as the result of the formation of basic salts the electroconductivity changes with time and the method does not seem to be sufficiently accurate. With time the electroconductivity can often change continuously as a result of the adsorption of ions on the precipitate which separates out. In order to elucidate the reasons for the change of electroconductivity with time during the titration of Zn ions with $Ba(OH)_2$ it is necessary therefore to exclude the effect of adsorption by precipitate ions. To do this, the titration of Zn should be carried out in the presence of some material which will be preferentially adsorbed on the precipitate which separates out before the Zn ions and the ions of the reagent added. $KMnO_4$ can be used for this purpose, since in its presence, as shown by preliminary experiments, a colored precipitate of zinc hydroxide and $BaSO_4$ can be obtained [2]. Consequently, during the conductometric titration of $ZnSO_4$ with $Ba(OH)_2$ in the presence of $KMnO_4$ it is to be expected that permanganate ions will be preferentially adsorbed on the precipitates of zinc hydroxide and $BaSO_4$ formed.

It was shown experimentally that on titrating solutions of $ZnSO_4$, addition of each portion of excess reagent leads to a continuous change in the electroconductivity after the equivalence point has been reached. This hampers the titration, and in the case of very weak solutions, makes titration impossible. If the $ZnSO_4$ is titrated in the presence of $KMnO_4$ the electroconductivity does not change with time. This fact is the basis of the method for the determination of Zn ions with $Ba(OH)_2$ described below.

30 ml of aqueous $ZnSO_4$ was placed in the vessel for conductometric titration, and a small amount of well washed, dry (old) $BaSO_4$ and 1-2 ml of a saturated $KMnO_4$ solution added. The solution was carefully stirred and conductometrically titrated with $Ba(OH)_2$. The $Ba(OH)_2$ was titrated against a solution of $ZnSO_4$ of known concentration (Table 1).

Aqueous solutions of $ZnSO_4$ can be titrated at concentrations of 0.01 N. At lower concentrations the experimental error increases considerably. It should be noted that when $ZnSO_4$ is titrated by the method described a change of the electroconductivity with time is still observed. This occurs when a lot of precipitate settles out and the amount of $KMnO_4$ is insufficient; in such a case the amount of $KMnO_4$ should be increased until it is considerably greater than the amount adsorbed on the precipitate which settles out. Only in such a case where adsorption of permanganate ions occurs will the change in concentration of these ions in the solution be small and not affect the magnitude of the electroconductivity.

When very dilute solutions of $ZnSO_4$ are titrated the electroconductivity can change with time as a result of the slow crystallization of the $BaSO_4$ precipitated. Results of titrations can be improved by the addition of dry $BaSO_4$, which will hinder the formation of super-saturated solutions.

The same method can be used for the titration of Zn-chloride, nitrate and acetate respectively, but the shape of the curves obtained will differ from that

obtained with $ZnSO_4$. When $ZnSO_4$ is titrated with $Ba(OH)_2$ the Zn ions separate from solution by forming a hydrated zinc oxide, while the SO_4 ions are removed as $BaSO_4$. As a result, up to the equivalence point the electroconductivity will drop rapidly. After the equivalence point, the Ba and OH ions appear and considerably increase the electroconductivity. The conductometric curve for $ZnSO_4$ will therefore have an acute angle. When Zn-chloride, nitrate or acetate are titrated with $Ba(OH)_2$, only the Zn ions are precipitated from solution, while instead of these the less mobile Ba ions are formed. In these cases, therefore, the electro conductivity will not drop so rapidly and the angle between the two branches of the curve will be obtuse, so that determination of the equivalence point by means of such a curve will be subject to rather large errors.

Titration of dilute solutions of Zn-chloride, nitrate or acetate is accompanied by a change in the electroconductivity with time, which hampers the determination of the equivalence point. Nevertheless, in the presence of $KMnO_4$, the equivalence point can still be found with a fair degree of accuracy as the results in Tables 2,3 and 4 show. Solutions of Zn-chloride, nitrate and acetate with concentrations less than 0.002 N can be titrated with an error of ca.1%. Cd and Cu interfere with the determination of Zn.

By this method solutions of $ZnSO_4$ containing small amounts of $CuSO_4$ can be titrated. In order to do this it is necessary to remove the Cu ions in the form of some insoluble compound, e.g. the iodide.

TABLE 1

$ZnSO_4$

Taken in mg	Found in mg	Error in %
20.94	20.91	0.2
15.70	15.67	0.2
10.47	10.80	3.1

TABLE 2

$Zn(CH_3COO)_2$

Taken in mg	Found in mg	Error in %
16.63	16.63	0.0
11.09	11.12	0.3
5.54	5.58	0.7
1.85	1.95	5.7

TABLE 3

$Zn(NO_3)_2$

Taken in mg	Found in mg	Error in %
11.97	11.97	0.0
7.18	7.19	0.2
1.19	1.21	1.7

TABLE 4

$ZnCl_2$

Taken in mg	Found in mg	Error in %
11.07	11.10	0.3
6.92	6.93	0.2
2.77	2.79	0.8

Before titrating solutions of $ZnSO_4$ containing $CuSO_4$, it is necessary to add another adsorbent instead of $KMnO_4$, viz.a saturated solution of methylene violet. A dry precipitate of $BaSO_4$ is also added. In order to avoid separation of free iodine, a few drops of Na-thiosulfate is added to the solution followed by a few drops of KI. The solution is subsequently stirred thoroughly and conductometrically titrated with $Ba(OH)_2$. Results are given in Table 5.

It has been previously observed that on titration of Zn-chloride, nitrate, or acetate with $Ba(OH)_2$, the respective Ba salt is formed. Being good electrolytes they considerably increase the electroconductivity of the solution at the equivalence point, so that the angle between the two branches of the conductometric curve becomes considerably greater than that of the conductometric curve for $ZnSO_4$. From this it follows that the angle between the two branches of the curve will be greater the higher the conductivity of the solution at the equivalence point. Therefore, in the titration of $ZnSO_4$ with $Ba(OH)_2$ in the presence of Cu ions, the angle between

the branches of the curve will increase since electrolytes (KI and $Na_2S_2O_3$) are added before titration which increase the electroconductivity at the equivalence point considerably. This in turn leads to a greater experimental error.

In cases where the $ZnSO_4$ solution contains large amounts of Cu it is necessary to increase the amount of thiosulfate and KI; this leads to an increase in the angle between the two branches of the conductometric curve and consequently to a greater experimental error. In order that the increase in experimental error be as small as possible, it is recommended that use of excess KI and $Na_2S_2O_3$ be avoided. The necessary amount can be determined by preliminary experiments. If titrations are made in the absence of methylene violet, low results are obtained.

Special attention should be given to the cleanliness of the titration vessel; care should be taken to remove precipitated Zn hydroxide and $BaSO_4$, which separates out on the walls and on the electrodes.

TABLE 5

Determination of Ni in Mixtures of Zinc and Copper Sulfates

Taken, in mg		Found Zn, in mg	Error, in %
Zn	Cu		
76.8	4.1	76.6	0.3
76.8	20.7	76.4	0.5
76.8	41.3	76.1	0.9
76.8	82.6	75.7	1.4

SUMMARY

A method for the titration of Zn salts with $Ba(OH)_2$ has been proposed. It has been established that in the titration of aqueous solutions of $ZnSO_4$ down to concentrations of 0.01 N, the electroconductivity changes with time after addition of the reagent, mainly because of the adsorption of ions of the added reagent and the precipitate formed. It has been shown that Zn can be titrated in the presence of small amounts of Cu.

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CONDUCTOMETRIC DETERMINATION OF POTASSIUM BY MEANS OF SODIUM PICRATE

V. V. Udovenko and G. B. Pasovskaya

Central-Asian State University, Tashkent

Potassium is usually determined by means of the chloroplatinate, perchlorate, and cobaltinitrite methods. Among other methods, the polarographic, colorimetric, and refractometric methods may be mentioned. The conductometric method is rarely used because the precipitate crystals form slowly, so that the electroconductivity of the solution changes with time over a prolonged period.

Of the conductometric methods for the determination of potassium known to us, the following may be mentioned. Jander and Pfundt [1] recommend titration of potassium conductometrically with sodium perchlorate at 0°. The authors note that the electroconductivity of the solution does not stabilize immediately after addition of the reagent, because of the slow crystallization of the precipitate.

Winkel and Maas [2] titrated potassium salts conductometrically with dipicrylamine. This was effected by precipitating the potassium by addition of a soluble dipicrylamine salt, dissolving the filtered precipitate in acetone, diluting with water to a final acetone concentration of 20-30% and titrating with 0.1 N HCl or 0.01 N naphthalene-α-sulfonic acid. The accuracy of their method was ±0.5%. It was noted that after addition of the first portion of acid the electroconductivity changed slowly with time because of the slow crystallization of the dipicrylamine which separated out. This change in the electroconductivity persisted until a sufficient number of crystals had formed, after which addition of reagent did not lead to a change of electroconductivity with time. It is possible to precipitate potassium by titrating it against a known amount of an aqueous solution of soluble salt of dipicrylamine, such as the magnesium salt. The filtrate containing excess of the soluble salt of dipicrylamine is then titrated with acid, when the dipicrylamine formed separates out as a precipitate.

Portnov and Afanasev [3] titrated potassium in an aqueous-alcoholic medium with a solution of fluosilicic acid conductometrically. The electroconductivity changed with time as a result of the slow formation of precipitate. The accuracy of this method was 2-2.5%. These authors changed the indirect method of Winkel and Maas for the determination of potassium. The accuracy varied from 0.6 to 1.5% according to the amount of potassium.

We propose that sodium picrate be used for the determination of potassium. Titration is carried out in aqueous solution, since preliminary experiments showed that titration in alcoholic solution did not improve the results.

The experimental method is briefly as follows. A known volume of the standard sodium picrate solution is placed in the vessel for titration, and a small amount of dry potassium picrate added. The test solution containing potassium chloride and sodium chloride is then added. The solution is carefully mixed and the excess sodium picrate backtitrated with potassium chloride of known strength. When this method is used the electroconductivity reaches its equilibrium value immediately after addition of the reagent.

The sodium picrate solution used as reagent was prepared by diluting a saturated solution of it to twice its volume with distilled water. The strength

of this solution was established by conductometric titration of a known volume of the sodium picrate solution with a solution of standard potassium chloride in the presence of a small amount of dry potassium picrate which is added to the solution.

Results obtained for the determination of potassium by the method described above (Table 1) show that the experimental error is approximately 2%. According to Table 2 any sodium chloride present does not interfere with the determination.

TABLE 1

Determination of potassium with sodium picrate

KCl		Error
Taken in mg	Found in mg	in %
56.20	56.00	0.4
80.30	79.30	1.2
105.50	105.59	0.08
120.58	122.23	1.3
150.72	152.53	1.2

TABLE 2

Determination of potassium in the presence of sodium

Taken in mg		mg KCl	Error
KCl	NaCl	found	in %
84.3	11.5	84.2	0.2
81.1	23.0	81.0	0.2
105.5	11.2	107.3	1.7
105.5	22.4	105.6	0.1
105.5	33.6	107.4	1.7
105.5	44.8	106.4	0.8
105.5	67.2	105.3	0.2

The method described can be used for mass determinations of potassium in different samples. A known weight of test sample is dissolved and, after separation of the accompanying cations, the alkali metals remaining are converted into the chlorides. The latter are dissolved in a small amount of distilled water and added to the sodium picrate solution. The excess sodium picrate is then determined as described above. The error of the method suggested for determination of potassium is of the same order as the fluosilicic and dipicrylamine methods. The advantages of this method are: a low temperature thermostat as used in the perchlorate method is unnecessary; no alcohol is required as in the fluosilicic method; no filtration is necessary as in the dipicrylamine method.

SUMMARY

A method is proposed for the determination of potassium by means of sodium picrate. The method consists in adding a known amount of test solution to a known amount of the reagent solution – sodium picrate – excess of which is back-titrated with potassium chloride. It has been shown that sodium ions present in the test solution do not interfere with the potassium determination.

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THE CHRONOMETRIC DETERMINATION OF ELECTROLYTE CONCENTRATIONS

1. DETERMINATION OF THE CONCENTRATIONS OF THIOSULFATE AND ACID IN THEIR REACTION MIXTURE

E. N. Ponomareva

Saratov Medical Institute

Many reactions in which organic materials participate proceed fairly slowly. In such cases it is expedient to carry out determinations on the concentration of reactants at definite time intervals from the amounts of reaction products formed. When a precipitate is formed it is very convenient to use a chronometric method for the determination of the concentrations of the organic reagents [1].

This method is also applicable for reactions between organic and inorganic compounds. Thus the reactions between aldehydes and ammonia [2] or methyl ketones with iodine [3,4] are used for this purpose. In such cases the quantitative determination of both the organic and mineral compounds is possible.

Nevertheless, the application of this rapid method for the determination of the concentration of only the mineral components during their mutual interaction has not yet been realized. The present communication is devoted to a number of investigations along these lines.

In order to develop our method of investigation we decided to concentrate on the reaction between thiosulfate and acid as being the most suitable for the purpose in view. When thiosulfate reacts with acid there is an induction period, as a consequence of which the turbidity which develops because of the formation of sulfur does not occur immediately. This time can be measured by a stop watch and consequently the chronometric principle can be used for the determination of the concentration of one of these reactants.

EXPERIMENTAL

Determination of the Concentration of Thiosulfate Solutions. Normal solutions of HCl and $Na_2S_2O_3$ were used as the base solutions. The other solutions used were prepared from these by dilution to the requisite concentrations.

The method used was as follows: 1 ml of the thiosulfate solution was mixed with 1 ml of acid and the time from the initiation of the reaction to the moment when turbidity appears was measured with a stop watch.

For increasing the accuracy of the results we used standard turbidities prepared as described by Nikitin and Vershinsky [5].

The results of the concentration of thiosulfate solutions as determined by reaction with hydrochloric acid are given in Table 1.

If the results given in Table 1 for the velocity with which the given mixtures become turbid are represented graphically, with the thiosulfate concentration along the X-axis (in g-equiv./liter) and the time from the beginning of the reaction to the onset of turbidity along the Y-axis, then turbidity isotherms are obtained as shown in Fig. 1.

However, if the inverse value of the thiosulfate concentration is used as in Nikitin's method [1], i.e. the degree of dilution, the turbidity isotherms of Fig. 1 assume a totally different form (Fig. 2).

TABLE 1

Rate with which Mixtures of Thiosulfate and Hydrochloric Acid become Turbid in Relation to Thiosulfate Concentration; t° = 14.5°

Expt. No.	Conc. of thiosulfate in g-equiv/liter	Turbidity velocity, in seconds					
		I	II	III	IV	V	Mean
1	1.000	9.6	9.2	9.0	9.4	9.2	9.30
2	0.833	10.8	10.8	10.6	10.6	10.6	10.70
3	0.750	12.8	12.2	12.0	11.8	12.2	12.10
4	0.666	13.3	13.3	12.2	13.0	13.0	13.14
5	0.500	17.3	17.5	17.0	17.0	17.2	17.20
6	0.417	20.7	20.3	20.8	20.4	20.4	20.50
7	0.375	22.8	22.8	22.4	22.2	22.3	22.50
8	0.333	25.3	25.6	25.0	25.4	25.2	25.30
9	0.250	34.0	33.4	32.3	34.0	32.9	33.50

Here (Fig.2) the value of z, which expresses the supplementary volume of solvent necessary to dilute the control (base solution), to a definite concentration is plotted horizontally.

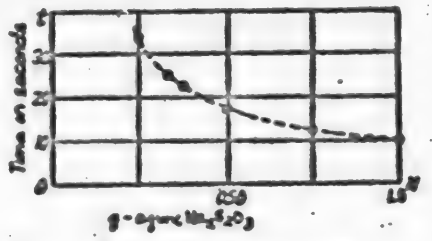

Fig.1. Turbidity isotherm for mixtures of HCl + $Na_2S_2O_3$.

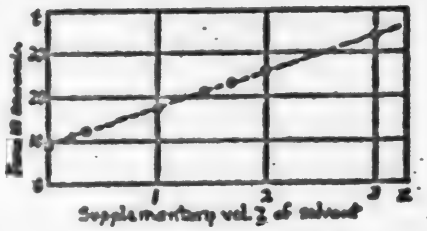

Fig.2. Turbidity isotherm for mixtures of HCl + $Na_2S_2O_3$ when degree of dilution is plotted along the composition axis.

If one volume of control solution is diluted n times, then the ratio of the concentration of this solution to the initial concentration is expressed by the relation:

$$\frac{c}{x} = n. \qquad (1)$$

This signifies that the volume z of the added solvent to give a definite dilution can easily be calculated from the relation

$$n = 1 + z. \qquad (2)$$

Results are given for the calculation of z for the solutions of Table 1, in Table 2.

These values of z are also plotted along the "composition" axis in Fig.2.

The linear form of the turbidity isotherm simplifies the method of determining the concentration of thiosulfate solutions [1]. We prepared a control (base)

solution of thiosulfate for which the velocity of development of turbidity t_1 was determined on interaction with acid. After dilution to twice its volume with water, the new velocity t_2 was determined. The velocity was then determined for a test solution in exactly the same way, t_x. From an equation for the straight line with two known points:

$$\frac{z - z_1}{z_2 - z_1} = \frac{v_x - v_1}{v_2 - v_1}, \qquad (3)$$

for $z_1 = 0$ and $z_2 = 1$, we get:

$$z = \frac{v_x - v_1}{v_2 - v_1}. \qquad (4)$$

TABLE 2

Calculated Values of z for Thiosulfate Solutions

Conc. of thiosulfate in g-equiv./liter	1.000	0.888	0.750	0.666	0.500	0.417	0.375	0.333	0.250
$z = n - 1$	0	0.20	0.33	0.50	1.00	1.42	1.67	2.00	3.00

Consequently, the value of z was determined from experimental results. By substitution in Equation (1) of the value of n from Equation (2), we get

$$\frac{c}{x} = 1 + z. \qquad (5)$$

The value of z from Equation (4) is substituted in Equation (5):

$$\frac{c}{x} = 1 + \frac{v_x - v_1}{v_2 - v_1}. \qquad (6)$$

From this we obtain the final equation for calculation of the concentrations:

$$x = \frac{c}{1 - \frac{v_x - v_1}{v_2 - v_1}}. \qquad (6a)$$

Results for determinations of the concentration of sodium thiosulfate solutions in reaction mixtures with hydrochloric acid are given in Table 3.

From this table it is clear that this rapid method which we have described for determining the concentration of sodium thiosulfate solutions gives completely satisfactory results. When other acids are used for this reaction, similar results were obtained.

Determination of Acid Concentration. In order to determine the order of the chemical reaction considered with respect to acid we carried out a number of experiments in which the acid concentration was varied. The results for the determination of the velocity of development of turbidity of the reacting mixtures are given in Table 4.

The results given in Table 4 are represented graphically in Fig. 3.

Fig. 3 was drawn in the same way as Fig.2, i.e. the degree of dilution by addition of z volumes of solvent was plotted along the composition axis. The isotherm obtained (Fig.3) shows that the change in concentration of acid from 4.0-0.0312 N has practically no effect on the reaction velocity (velocity of development of turbidity); the isotherm is parallel to the abscissa for the concentrations indicated. It is only below concentrations of 0.0312 N that the

straight line isotherm starts to curve upwards steeply.

This break in the curve occurs at ratios of acid to thiosulfate not greater than 0.03 equiv. to 1 equiv thiosulfate.

Thus, determination of acid by this method (i.e. by reaction with thiosulfate) is possible only in those cases where the concentration of thiosulfate will be several times greater than that of the acid.

If a solution 0.0312 N with respect to acid is used as the base sol for lower concentrations, it is easy to determine the concentration of the acid by the velocity of turbidity development by reacting the solution with thiosulfate. Results for the determination of hydrochloric acid concentration by reacting solutions with thiosulfate are given in Table 3.

TABLE 3

Relative Errors in the Determination of the Concentration of Thiosulfate Solutions

Expt. No.	Concentration of thiosulfate taken in g-equiv/liter	Concentration of thiosulfate found in g-equiv/liter	Relative error
1	1.000	Blank 1	
2	0.832	0.850	+2.04
3	0.750	0.728	-1.60
4	0.666	0.673	+1.05
5	0.500	Blank 2	
6	0.418	0.414	+0.24
7	0.375	0.374	-0.27
8	0.338	0.330	-0.9
9	0.250	0.246	-1.6

TABLE 4

Rate with which Mixtures of Thiosulfate and Hydrochloric Acid become Turbid in Relation to Acid Concentration. t = 19°

Expt. No.	Concentration of acid in g-equiv./liter	Turbidity velocity in seconds			
		I	II	III	Mean
1	4.00000	6.0	6.2	6.0	6.0
2	2.00000	6.0	5.9	6.0	6.0
3	1.00000	6.3	6.1	6.0	6.1
4	0.50000	7.0	6.4	6.6	6.7
5	0.25000	7.0	7.0	6.0	6.3
6	0.12500	6.5	6.9	6.8	6.7
7	0.06250	7.2	7.4	6.9	7.2
8	0.03120	7.2	7.2	6.6	7.0
9	0.01560	8.8	8.9	9.0	8.8
10	0.00780	12.2	11.8	12.4	12.2
11	0.00390	20.0	20.3	18.7	19.9
12	0.00195	34.0	33.2	32.8	33.3

SUMMARY

1. The reaction velocity between thiosulfate and acid in relation to the concentrations of the components was studied by a chronometric method.

TABLE 5

Results of the Chronometric Determination of Concentrations of Acid by Reaction with Thiosulfate

Expt. No.	Concentration taken in g-equiv/liter	Concentration found in g-equiv/liter	Relative error in %
1	0.03120	Blank 1	
2	0.01560	Blank 2	
3	0.00780	0.00800	+2.5
4	0.00390	0.00382	−2.0
5	0.00195	0.00200	+3.0

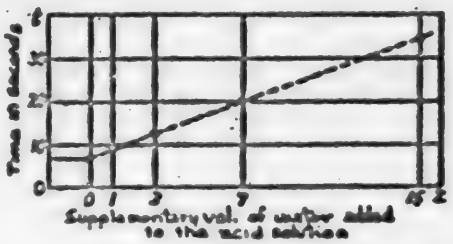

Fig. 3. Turbidity isotherm for HCl + $Na_2S_2O_3$ mixtures when dilutions of the acid solution are plotted on the composition axis.

2. The turbidity isotherms obtained have been investigated and their analytical applications indicated.

3. A characteristic of the reaction was discovered, viz. that up to a certain concentration limit the reaction is of zero order with respect to acid.

4. The method described for the determination of electrolyte concentration can be used for all reactions for which an induction period can be observed. i.e. the time from the beginning of the reaction to the development of turbidity, or color, etc.

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CHRONOMETRIC DETERMINATION OF ELECTROLYTE CONCENTRATIONS

2. DETERMINATION OF SULFITE AND IODATE CONCENTRATIONS IN THEIR ACIDIFIED REACTION MIXTURES

E. N. Ponomareva

Saratov Medical Institute

In our first paper [1] we showed how a rapid chronometric method for the determination of turbidity [2,3] could be applied to the determination of electrolyte concentrations in the case of sodium thiosulfate and hydrochloric acid. In a determination of this kind, the time is measured (by means of a stop watch) from the beginning of the reaction to the moment at which turbidity is first manifested as the result of the formation of sulfur and the concentrations calculated from a special equation.

The chronometric method can also be used for the quantitative determination of electrolytes in colored reactions, where the time from the beginning of the reaction to a moment at which a definite color starts to develop can be measured with a stop watch. One of the reactions of this type which is of particular importance is that between HIO_3 and H_2SO_3. This reaction has been studied from the point of view of its mechanism and its external effects by Landolt [4]. This valuable reaction has a considerable induction period (the length of time from the beginning of the reaction to the appearance of free iodine); the iodine slowly turns starch blue.

The final result of a number of reactions is

$$5H_2SO_3 + 2HIO_3 = 5H_2SO_4 + H_2O + I_2.$$

The separate stages of which are as follows:

1) $3H_2SO_3 + HIO_3 = 3H_2SO_4 + HI$;

2) $5HI + HIO_3 = 3H_2O + 3I_2$;

3) $H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$.

This implies that iodine can only be liberated in significant amounts when the H_2SO_3 has already been used up. Thus iodine is evolved (colors the starch) only when there is a sufficient excess of HIO_3 as an oxidizing agent. The time from the beginning of the reaction to the moment when the mixture becomes colored (the mixture becomes colored throughout its volume simultaneously) can be very accurately measured with a stop watch; the induction period depends both on the concentration of HIO_3 and H_2SO_3 and on other factors.

As far as we know no investigator has used this reaction for analytical purposes. In our opinion, nevertheless, it can be used for the quantitative determination of the original reactants themselves and of other compounds.

What it amounts to is that any substance which can participate in the oxidation-reduction process can affect the induction period of the reaction. The induction period will vary according to the amount of the compounds added. The study of the effect of the concentration of these added compounds is the chief purpose of this investigation.

On practical grounds we thought it more expedient to use KIO_3 and Na_2SO_3 in preference to the free acids (HIO_3 and H_2SO_3).

Since the reaction between the anions IO_3^- and SO_3^{2-} is only possible in acid media, we first studied the effect of different concentrations of H_2SO_4 on the reaction velocity. In addition it was necessary to determine the effect of the concentrations of the reactants themselves.

The present paper is devoted to a description of the effect of H_2SO_4, KIO_3 and Na_2SO_3 on the induction period. A chronometric method for the determination of KIO_3 and Na_2SO_3 in solution is suggested.

EXPERIMENTAL

Effect of Acid Concentration on the Reaction Velocity. The part played by acid in this reaction is not restricted to the process of liberating H_2SO_3 and HIO_3, since the hydrogen ion concentration should also be of considerable importance in exerting a catalytic effect on the reaction. Thus, in the determination of Cl^-, together with Br^- and I^- with $NaBrO_3$ in the presence of H_2SO_4 by Berg's method [5], when 1.5 N H_2SO_4 is used only the Br^- and I^- ions are oxidized, while only a small proportion of the Cl ions are oxidized. It should be noted that at this high concentration of H_2SO_4, the optimum concentrations of the halides themselves in this determination lie within the limit 0.01-0.1 N [5].

We prepared 0.002 M aqueous solutions of KIO_3 and 0.005 M aqueous solutions of Na_2SO_3. The H_2SO_4 solutions vary from 0.5-0.3125 N. All solutions were prepared with doubly distilled water. The reaction was carried out as follows: 1 ml of KIO_3 solution was mixed in a test tube with 1 ml of Na_2SO_3 solution and 2 drops of starch solution; to this mixture was added 1 ml of the H_2SO_4 solution. After shaking the mixture for some time a blue color suddenly appears throughout the volume of the liquid. The time from the beginning of the reaction, i.e. from the moment when acid is added, to the time when color first appears was measured with a stop watch. Since the time taken to add the acid from pipette to test tube has a considerable effect on the accuracy of the measurements, we used a special pipette for introducing the acid whereby the acid was always blown into the reaction mixture with the same velocity.

TABLE 1

The Effect of Sulfuric Acid Concentration on the Reaction Velocity between Potassium Iodate and Sodium Sulfite

Expt. No.	Conc. of H_2SO_4 in mole/liter	Induction period in seconds			
		1	2	3	Mean
1	0.50000	6.8	6.8	6.7	6.76
2	0.25000	11.8	11.7	11.8	11.76
3	0.12500	20.6	20.2	20.5	20.43
4	0.06250	36.8	36.8	37.0	36.87
5	0.03125	68.8	69.0	68.8	68.87

Results for the measurement of the induction period for different acid concentrations are given in Table 1.

By a comparison of the induction periods for this reaction at different concentrations of H_2SO_4, it can be concluded that the reaction velocity is linearly related to the acid concentration.

Effect of the Iodate Concentration. Since the reaction between H_2SO_3 and H_2SO_3 proceeds according to the equation

$$5H_2SO_3 + 2HIO_3 = 5H_2SO_4 + I_2 + H_2O,$$

it follows that the molar ratio of sulfite to iodate is of decisive importance in this case. On increasing this ratio no iodine at all is evolved. The reaction will proceed only for such changes in the concentration of reactants for which the molar ratio of sulfite to iodate will decrease. This means that there are only two possibilities: to decrease the concentration of sulfite for a constant iodate concentration; or to increase the iodate concentration from the critical molar ratio for a constant sulfite ratio.

In Landolt's work on the study of the velocity of this particular reaction some experimental data is given on this question which is of interest to us. This author in his study of the law of mass action for this reaction, changed the concentration of HIO_3, while leaving the H_2SO_4 concentration constant throughout.

For our analytical purposes we examined the relations between the values of the HIO_3 concentrations in Landolt's experiments and the induction periods which he observed for the respective solutions. Since the induction period in a given case is not related by a simple expression to the concentration of the HIO_3, in our calculations we used a method proposed previously by Nikitin in his colorimetric investigation of the reaction velocity of the condensation of carbonyl compounds [6]. He used the equation:

$$\frac{x}{c} = \left(\frac{h_c}{h_x}\right)^n, \qquad (1)$$

where h is the height on the colorimeter scale, i.e., the reciprocal of the intensity. Having established the value of the index n for the reaction he studied, Nikitin derived the corresponding equations for calculating the requisite concentrations.

The molar concentrations of HIO_3 (for constant concentration of H_2SO_4) and the values of the respective induction periods from Landolt's paper are reproduced in Table 2. In addition the values of n which were calculated from the equation below are given:

$$\frac{c_1}{c_2} = \left(\frac{t_2}{t_1}\right)^n, \qquad (2)$$

from which

$$n = \frac{\log c_1 - \log c_2}{\log t_2 - \log t_1}. \qquad (3)$$

TABLE 2

Comparison of the Induction Periods of Solutions with Different Concentrations of HIO_3

Expt. No.	Concentration in mole/liter·10^3		Induction period for comparable solutions		$n = \frac{\log c_1 - \log c_2}{\log t_2 - \log t_1}$	Average value of n
	c_1	c_2	t_1	t_2		
1	2.226	3.338	55.98	28.36	0.595	0.60
2	2.226	4.450	55.98	17.80	0.604	
3	2.226	5.562	55.98	12.24	0.602	
4	2.226	6.673	55.98	9.08	0.603	
5	2.226	7.783	55.98	7.07	0.609	
6	2.226	8.893	55.98	5.55	0.599	

Consequently the value of n necessary for calculating the concentration of HIO_3 has a mean of ca.0.6 and the equations for calculating the concentration will therefore be of the form

$$x = c\left(\frac{t_c}{t_x}\right)^{0.6} \qquad (4)$$

where t_c is the induction period of the control solution; t_x is the induction period of the test solution.

The concentrations of HIO_3 actually used by Landolt and those calculated by means of the above equation are compared in Table 3.

TABLE 3

Accuracy of the Determination of Concentrations of HIO_3

Expt. No.	Molar conc. of HIO_3 taken	Induction period in seconds	Calculated conc. of HIO_3	Relative Error in %
1	3.338	28.36	3.348	+0.20
2	4.450	17.18	4.413	-0.83
3	5.562	12.34	5.542	-0.36
4	6.673	9.08	6.630	-0.64
5	7.783	7.07	7.705	-1.00
6	8.893	5.55	8.906	+0.15

As these results show, the concentrations of HIO_3 calculated by means of the above equation are very close to the actual concentrations of the solution; the relative error varies from +0.3 to -1.0%.

In our experiments we varied the concentration of KIO_3 while keeping the H_2SO_4 concentrations constant at 0.025 M and the Na_2SO_3 constant at 0.01 M.

The values of the induction periods (the reciprocals of the reaction velocity) in the reaction mixtues of KIO_3, Na_2SO_3 and H_2SO_4 for changes of KIO_3 concentration at 20° are given in Table 4.

TABLE 4

Effect of the Concentration of KIO_3 on the Induction Period in Mixtures with Sulfite in the Presence of Acid, at 20°

Expt. No.	Iodate conc. in mole/liter	Induction Period in seconds			
		1	2	3	Mean
1	0.01800	10.5	10.4	10.6	10.5
2	0.01350	14.2	14.2	14.2	14.2
3	0.00900	21.5	21.2	21.2	21.3
4	0.00675	29.5	28.8	29.8	29.7
5	0.00450	46.5	46.6	46.2	46.4

Results for the determination of n necessary for the calculation of the KIO_3 concentrations are given in Table 5.

This table shows that the average value of n at the given temperature is 0.95. Therefore for the solutions of KIO_3 in Table 5 the concentrations can be calculated by means of the equation

$$x = c\left(\frac{t_c}{t_x}\right)^{0.95}. \qquad (5)$$

The results of these calculations are given in Table 6. A KIO_3 solution with concentration 0.018 M was used as the control solution.

TABLE 5

Comparison of Induction Periods for Solutions with Different Concentrations of KIO_3

Expt. No.	Molar concentration of comparable iodate solutions		Induction period for comparable solutions		$n = \frac{\log c_1 - \log c_2}{\log t_2 - \log t_1}$	Mean value of n
	c_1	c_2	t_1	t_2		
1	0.01800	0.01350	10.5	14.2	0.95	
2	0.01800	0.0090	10.5	21.3	0.98	0.95
3	0.01800	0.00675	10.5	29.7	0.94	
4	0.01800	0.00450	10.5	46.2	0.93	

TABLE 6

Accuracy of the Determination of Concentrations of Iodate

Expt. No.	Molar concentration of KIO_3 taken	Induction period in seconds	Calculated molar conc. KIO_3	Relative error, %
1	0.01350	14.2	0.01352	+0.15
2	0.00900	21.3	0.00919	+2.11
3	0.00675	29.7	0.006704	-0.74
4	0.00450	46.4	0.00440	-2.22

TABLE 7

Reaction Velocity of Iodate with Sulfite in Acid Media in Relation to the Sulfite Concentration at 20°

Expt. No.	Concentration of sulfite in mole/liter	Induction period in seconds			
		1	2	3	Mean
1	0.00600	31.2	31.6	31.8	31.5
2	0.04500	35.2	34.8	35.0	35.0
3	0.00300	40.2	40.6	40.0	40.2
4	0.00225	45.2	45.2	44.8	45.1
5	0.00150	52.6	52.0	52.2	52.2

Effect of Sulfite Concentration. A 0.006 M solution of Na_2SO_3 was prepared as the base solution and other solutions of different concentrations prepared from it by dilution.

The concentrations of the H_2SO_4 and KIO_3 solutions were 0.05 and 0.004 M, respectively. The method adopted was as before (equal volumes in a test tube).

The induction periods for different solutions of Na_2SO_3 are given in Table 7, while the respective values of n used in the equation for calculating the Na_2SO_3 concentrations are given in Table 8.

A comparison of the values of n obtained for the Na_2SO_3 solutions shows only a small deviation from the mean value of 2.76.

The concentrations of Na_2SO_3 calculated according to Equation (6) given below, for the solutions prepared by dilution of the Na_2SO_3 control solution are given in Table 9.

$$x = c\left(\frac{t_c}{t_x}\right)^{2.76} \qquad (6)$$

TABLE 8

Comparison of the Induction Periods for Different Sulfite Concentrations

Expt. No.	Molar conc. of comparable solutions of sulfite		Induction period for comparable sulfite solutions		$n = \frac{\log c_1 - \log c_2}{\log t_2 - \log t_1}$	Mean value of n
	c_1	c_2	t_1	t_2		
1	0.00600	0.00450	31.5	35.0	2.727	
2	0.00600	0.00300	31.5	40.2	2.843	2.76
3	0.00600	0.00225	31.5	45.1	2.732	
4	0.00600	0.00150	31.5	52.2	2.744	

TABLE 9

Accuracy of the Determination of Sulfite Concentrations

Expt. No.	Molar conc. of sulfite taken	Induction period in seconds	Calculated conc. of sulfite	Relative error, %
1	0.00450	35.0	0.004485	-0.33
2	0.00300	40.2	0.003060	+2.00
3	0.00225	45.1	0.002230	-0.89
4	0.00150	52.2	0.001490	-0.67

All these results show that the chronometric method described above can be used to determine the concentrations of iodate and sulfite in their acidified reaction mixtures fairly accurately.

The value of n determined for substitution in the equation for calculating the concentrations of KIO_3 and Na_2SO_3 can of course be changed according to the conditions. The concentration of H_2SO_4, the molar ratio of KIO_3 to Na_2SO_4, and the temperature all affect the value of n. n must therefore be determined independently in each individual case, by using two control solutions of the salt to be determined, the concentration of one of these solutions being twice that of the other.

Let the concentration of control solution 1 be c_1, that of control solution 2 be c_2. Then from Equation (2) the value of n is calculated (see Equation 3). By substituting $c_1/2$ for c_2 we get:

$$n = \frac{\log 2}{\log t_2 - \log t_1} \qquad (7)$$

and

$$n = \frac{0.301}{\log t_2 - \log t_1} \qquad (7a)$$

If the value of n derived from Equation (7a) is substituted in Equation (2) we finally get the equation for calculating the concentration of the salt to be determined.

$$x = c\left(\frac{t_1}{t_x}\right)^{\frac{301}{\log t_2 - \log t_1}} \qquad (8)$$

where c is the concentration of the control solution; t_1 the induction period of the control solution before dilution and t_2 the induction period of the same control solution after dilution with an equal volume of water; t_x the induction period for the test solution.

The methods for the determination of concentration of additives (different salts) will be described in a further communication.

SUMMARY

1. The reaction velocity between KIO_3 and Na_2SO_3 in the presence of H_2SO_4 has been studied with respect to the H_2SO_4 concentration.

2. The effect of the concentrations of KIO_3 and Na_2SO_3 respectively on the induction period of the reaction has been investigated.

3. The analytical significance of this reaction for the chronometric determination of the concentrations of KIO_3 and Na_2SO_3 in their reaction mixtures has been pointed out.

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THE INTERMEDIATE POTENTIAL JUMP DURING THE POTENTIOMETRIC TITRATION OF SOLUTIONS OF ALUMINUM SALTS WITH SODIUM FLUORIDE

I. L. Teodorovich

Central Asian State University, Tashkent

When solutions of aluminum salts are titrated with NaF a small intermediate potential jump is observed after the addition of from $\frac{1}{3}$ to $\frac{1}{4}$ of the equivalent amount of NaF solution. This phenomenon has not been theoretically explained [1]. In the presence of Mg^{2+} this jump is more pronounced. Polyak [2] noticed that if at the point when a potential jump is observed, a few drops of very dilute acid are added, then the former potential is established, while subsequently the potential changes more rapidly in the neighborhood of the equivalence point. We have made it our aim to try and explain this phenomenon.

EXPERIMENTAL

A compensating circuit with a mirror galvonometer was used ($2.4 \cdot 10^{-9}$ A/mm/M). A platinum ferro-ferri electrode served as the indicator while a saturated calomel electrode was used as the auxiliary electrode.

All the reagents used $KAl(SO_4)_2 \cdot 12H_2O$, NaCl, ethyl alcohol, $FeCl_2$[1)], $FeCl_3$, and quinhydrone were chemically pure. Chemically pure NaF was freed from Na_2SiF_6 by Tananaev's method [3]. Firstly, parallel titrati ns were made of 4.85 ml of a 0.0332 M solution of $KAl(SO_4)_2$ with 0.1073, 0.2146, 0.4291 M solutions of NaF respectively in an aqueous-alcohol medium saturated with NaCl and with the addition of a small amount of $FeCl_2$ and $FeCl_3$ [1]. The $KAl(SO_4)_2$ was standardized by potentiometric titration with a standard solution of NaF.

TABLE 1

Position of the intermediate potential jump during titrations with NaF. 4.85 ml of 0.0332 M $KAl(SO_4)_2$, and 5 ml C_2H_5OH, 4 g NaCl taken.

Expt. No.	Molarity of NaF solution A	NaF solution used in ml				Ratio $\frac{C}{D}$
		Up to the beginning of the intermediate potential jump B	Up to the end of the intermediate potential jump C	Diff. C − B	For all the titration D	
1	0.1073	2	3	1	8.90	~1/3
2	0.2146	1	1.5	0.5	4.55	~1/3
3	0.4291	0.5	0.8	0.3	2.25	~1/3

Results given in Table and Fig. 1 show that the appearance of the intermediate potential jump corresponds in all cases to the consumption of approximately equal amounts of NaF (ca. $\frac{1}{3}$ of the equivalent wt.).

It is known that in this method [1] the potential jump at the platinum

1) $FeCl_2$ contains some Fe^{3+}.

electrode towards the end of the titration after the quantitative formation of AlF_6^{3-}, is determined by the sharp decrease in the ratio $\frac{[Fe^{3+}]}{[Fe^{2+}]}$ as the result of the formation of FeF_6^{3-}; the latter cannot be formed in the initial stages of the titration when a large amount of the Al is not yet combined. Consequently it is necessary to explain the intermediate potential fall (jump) by some other process, viz. the pH change as shown by a number of experiments. This was confirmed by titrating of the Al salt with a solution of NaF using a quinhydrone electrode (without addition of $FeCl_2$ and $FeCl_3$); in this case also an intermediate potential jump can be observed, which corresponds to the pH[1] change (Fig. 2 and Table 2).

TABLE 2

Change of pH during the titration with the given quinhydrone electrode. 4.85 ml of 0.031 M $KAl(SO_4)_2$, 5 ml of C_2H_5OH, 4 g NaCl taken. Titration carried out with 0.1080 M NaF

Expt. No.	NaF used in ml	E.M.F. in Volts	pH of solution	Conc. of $[H^+]$ in g-ions/liter
1	0	0.2794	2.95	$1.12 \cdot 10^{-3}$
2	0.5	0.2754	3.02	
3	1.0	0.2684	3.13	
4	1.5	0.2594	3.28	$5.25 \cdot 10^{-4}$
5	2.0	0.2374	3.65	
6	2.3	0.2284	3.80	
7	2.6	0.2204	3.94	$1.15 \cdot 10^{-4}$
8	3.0	0.2124	4.07	
9	3.5	0.2064	4.17	
10	4.5	0.1974	4.32	
11	5.5	0.1908	4.43	
12	6.5	0.1804	4.60	
13	7.0	0.1743	4.71	
14	7.5	0.1644	4.87	$1.35 \cdot 10^{-5}$
15	8.0	0.1474	5.16	
16	8.2	0.1414	5.26	
17	8.3	0.1044	5.88	
18	8.4	0.0714	6.43	
19	8.5	0.0567	6.68	$2.09 \cdot 10^{-7}$
20	8.6	0.0479	6.81	
21	8.8	0.0433	6.91	
22	9.3	0.0442	6.84	
23	9.8	0.0397	6.97	

Note: Conc. of $[H^+]$ is assumed to be the same as the activity ($t° = 27.5°$).

Discussion of Results

According to I. V. Tananaev [4] when a solution of NaF is added to the Al salt, a stepwise reaction takes place:

$$Al^{3+} \longrightarrow AlF^{2+} \longrightarrow AlF_2^{+} \longrightarrow AlF_3,$$

or more fully: $AlCl_3 \longrightarrow AlFCl_2 \longrightarrow AlF_2Cl \longrightarrow AlF_3$.

1) The pH value was calculated as usual without taking into account the potential jump on the boundary, water-water alcohol, and the possible effects of Al^{3+} on the quinhydrone.

According to Greenberg [5] AlF_3 is more stable than $AlCl_3$, and simple Coulomb forces play an essential part in the stability of the internal bonds. This fact enables one to calculate approximately the energy of formation (in conventional units [6]) in the series:

$$AlCl_3{}^{I} - AlFCl_2{}^{II} - AlF_2Cl{}^{III} - AlF_3.$$

This calculation confirms the increasing stability of the compounds in the series from $AlCl_3$ to AlF_3 and consequently of a diminishing tendency to hydrolyze. The three stages I, II, III should therefore correspond to the three potential

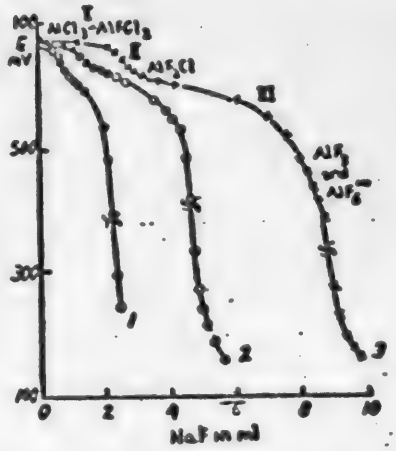

Fig. 1. Titration curves for 4.85 ml of 0.0332 M $KAl(SO_4)_2$ with a ferri-ferro-electrode. 1) 0.429 M; 2) 0 2146 M; 3) 0.1073 M solutions of NaF.

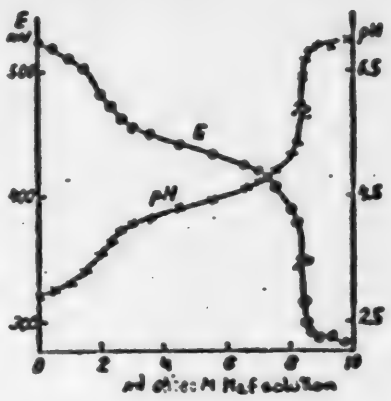

Fig. 2. Titration curve for 4.85 ml of 0.031 M $KAl(SO_4)_2$ with 0.1080 M NaF using a quinhydrone electrode.

drops (acidities), the value of which increases from I to III; this is confirmed by the form of the titration curves (Figs 1 and 2) and by the experimental results given in Table 3, which were obtained by working out the figures in Table 2. The potential fall in stage I (total final product $AlFCl_2$) cannot be sharp, because it is smoothed out by hydrolysis of $AlFCl_2$, the potential fall in stage II (final product AlF_2Cl) is steeper because it is not smoothed out to such an extent by the hydrolysis of AlF_2Cl (this hydrolyzes less easily than $AlFCl_2$); the potential fall in the final stage, stage III (final product AlF_3 and Na_3AlF_6) is the most significant because there is practically no Al compound left, the hydrolysis of which could to some extent hinder the fall of acidity of the solution.[1] The large section (almost horizontal) of the curve at stage III is explained by the total formation of AlF_3 and Na_3AlF_6.

The amount of NaF which corresponds to the intermediate potential jump is approximately $\frac{1}{3}$ of the equivalent amount of NaF, and corresponds to the formation of AlF_2^+ (stage II) as a stage in the total reaction:

$$Al^{3+} + 6F^- \longrightarrow AlF_6^{3-}$$ [1]

($\frac{2}{6} = \frac{1}{3}$)[2]

In this way the intermediate potential jump (or fall) during titration of

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[1]) Of course in the presence of Fe^{3+} and Fe^{2+} the potential should drop sharply as the result of the formation of FeF_6^{3-}.

[2]) As suggested by Kh. B. Medinsky.

solutions of Al salts with NaF is explained by the exhaustion of all the $AlFCl_2$ (AlF^{2+} and $AlFCl^+$ ions) and the quantitative formation of AlF_2Cl (AlF_2^+ ions). This enables one to explain Polyak's observation [2] that the addition of a small amount of acid at the moment when the potential jump is observed, compensates the lowering of acidity at this point, i.e. increases the potential of the platinum electrode. In view of this, the formation of AlF_6^{3-} also proceeds at a higher potential, while the jump $\frac{\Delta E}{\Delta V}$ becomes sharper, because there is a smaller amount of acid present to hinder the hydrolysis of $FeCl_3$ and at the same time increases the concentration of Fe^{3+}, which determines the sharper final potential jump.

The increase in the sharpness of the intermediate potential jump in the presence of Mg^{2+} can be explained by the fact that $MgCl_2$, e.g., is hydrolyzed to a greater extent than MgF_2 and even MgFCl, so that according to the amount of F^- added to the Mg^{2+}, the pH of the solution should increase.[1)]

TABLE 3

Relative fall in acidity during titration of $KAl(SO_4)_2$ with an NaF solution

Index Nos. of points from Table 2	Stage of the reaction between corresponding points. Graph 1	$\frac{c_{H_a^+}}{c_{H_b^+}} = 1$	∂V in ml	$\frac{1}{\partial V}$
1-4	$AlCl_3 - AlFCl_2$	$\frac{c_{H_1^+}}{c_{H_4^+}} = \frac{1.12 \cdot 10^{-3}}{5.25 \cdot 10^{-4}} = 2.1$	1.5	1.5
4-7	$AlFCl_2 - AlF_2Cl$	$\frac{c_{H_4^+}}{c_{H_7^+}} = \frac{5.25 \cdot 10^{-4}}{1.15 \cdot 10^{-4}} = 4.6$	1.1	4.1
14-19	$AlF_2Cl - AlF_3$	$\frac{c_{H_{14}^+}}{c_{H_{19}^+}} = \frac{1.35 \cdot 10^{-3}}{2.09 \cdot 10^{-7}} = 64.3$	1	64.3

Note. $c_{H_a^+}$ and $c_{H_b^+}$ are concentrations corresponding to the points on Graph 1; ∂V is the amount in ml of fluoride solution added in the interval between points on Graph 1.

The practical significance of this intermediate potential jump is that its appearance enables one to foresee the position of the final titration end point, and in rapid analysis to determine approximately the amount of aluminum.

SUMMARY

1. It has been shown that the form of the curve obtained by titrating Al salts with NaF using a ferri-ferro electrode is determined by the potential fall in the platinum electrode as a result of an increase in pH and a decrease of the ratio $[Fe^{3+}]/[Fe^{2+}]$ in solution.

2. A theoretical explanation is advanced for the titration curve on the basis of the increase in stability of the compounds in the following series in going from left to right: $AlCl_3 \longrightarrow AlFCl_2 \longrightarrow AlFe_2Cl \longrightarrow AlF_3$.

3. It has been shown that the intermediate potential jump (fall) is explained by the formation of AlF_2Cl (AlF_2^+ ions), whereby the acidity of the solution decreases, giving rise to a potential fall on the platinum electrode.

1) pH ~ 0.1 M $MgCl_2$ < 7 [7] pH of saturated MgF_2 (0.013 g/100 g solution) > 7 [8].

4. It was found that the position of the intermediate potential jump on the titration curve enables the position of the final end point to be forecast when solutions of Al salts are titrated with NaF. In rapid analysis therefore the amount of Al can be estimated approximately by titrating only as far as the potential jump, thereby decreasing the titration time.

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A NEW METHOD OF CONSTRUCTING A BLACKENING CURVE AND ITS USE IN X-RAY CHEMICAL ANALYSIS

E. E. Vainshtein and N. V. Turanskaya

Institute for Geochemistry and Analytical Chemistry, Acad. Sci. USSR Moscow

Quantitative X-ray spectral analysis using photographic registration assumes a knowledge of the blackening curve,[1)] which have been constructed either by one of the methods described in standard text books [1,2] or by the method worked out recently by Protopov [3]. In the present communication a new method is described for constructing a blackening curve, which differs from the others in its simplicity and its convenience for use in quantitative X-ray spectral analysis. Work carried out in our laboratory showed that by means of this method analyses could be carried out more rapidly and with greater accuracy. The basic idea is as follows. Any method of constructing a blackening curve is based on the comparison of two series of numbers; one characterizing the laws of the changes in intensity of the spectral lines and the other composed of the values for blackening which correspond to each of the points of the first series. The only essential difference between the other methods used hitherto for constructing blackening curves is in the manner in which the investigator interprets the law of intensity changes for the lines used in constructing the curve. In some cases this is achieved by regular weakening of the initial intensity of the lines by means of a special wedge absorber, while in others the intensity of the lines are left unchanged and "intensity marks" are superimposed on the spectrogram by varying the time for which the points on the spectrogram are illuminated.

In the method described here it is proposed to use as the initial intensity series, values which correspond to individual points on the contours of the X-ray spectral lines, particularly those which are symmetrical, and can be described by a dispersion formula. Such lines [5] e.g. are the $K\alpha_{1,2}$ doublets of practically all the elements the atomic numbers of which, Z, are greater than 30.

The intensity of separate points within the limits of the contours of each of these lines is related to the width of the lines at a given cross section by the simple equation [5]:

$$x = \Gamma \sqrt{n - 1} \qquad (1)$$

where n is the ratio of the intensity of the line at its maximum to the value at some arbitrary point on the contour; x is the width of the line at this cross section and Γ is the so-called half width. The applicability of (1) to different classes of X-ray spectral lines was verified experimentally and was used for studying the form of the $K\alpha_{1,2}$ doublets of different elements forming components of chemical compounds and alloys [5]. It, i.e. (1), can be used for solving the

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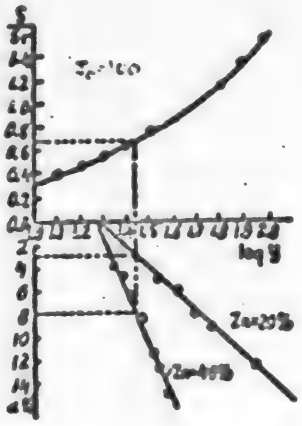
1) In those cases [4] where construction of the blackening curve in an explicit manner is essential for carrying out analyses, it is necessary to use a number of coefficients obtained empirically, the relation of which to the content of the element to be analyzed is determined by the absence of proportionality between the blackening of the lines on the spectrogram and their intensity.

problems which are the subjects of the present communication. For this purpose we consider those changes in the form of the symmetrical X-ray spectral line which occur during its registration on the X-ray plate. To each point of the original contour mapped out on the intensity scale there will correspond a definite point on the experimentally registered (on the blackening scale) profile of the spectral line. One curve is transformed into the other. The law which governs this transformation is the required relation between blackening and intensity. It is different for different types of photographic material. In practice, however the possibility of a reverse transformation from the known form of the line on the blackening scale to its contour on the intensity scale is important. Such a transformation can be easily realized, if it is taken into account that independently of the concrete form of the law of transformation of one curve into the other[1], two symmetrical points on both curves (corresponding to one value of the blackening or intensity) should remain equidistant. This enables one, having measured the width of the line at any given section of the experimental profile (on the blackening scale), by means of equation (1) to find the value n on the true profile of the line (on the intensity scale) which corresponds to a given value of the blackening.

In order to do this only the value of Γ relating to the true profile of the spectral line is necessary.



In the simplest case, when the spindoublet is used for the construction of the blackening curve, the value of Γ can be easily determined. In view of what was stated above it should be equal to the width of the experimental line K_{α_1}, measured for a blackening value on its profile, which is equal to the value of the blackening at the maximum for line K_{α_2}. The intensity of the latter line is known to be approximately equal to half of the intensity of K_{α_1} and does not depend on the experimental conditions.

In the general case when the singlet lines are used, the experimental determination of Γ can be carried out by means of measurements made on lines, a part of the length of which is artificially weakened by absorption in an aluminum foil of an arbitrary but known thickness.

Thus, to each arbitrarily selected value of blackening on the experimental profile of K_{α_1} lines it is possible to assign a corresponding intensity value, expressed on an arbitrary scale, which corresponds to the intensity of the line at its maximum (I_0). This is the required relation $S = S(I)$; its form should not depend on the chemical nature of the element, the $K_{\alpha_{1,2}}$ line of which is selected for constructing the curve[2] for the compound into whose composition the element enters[3]. Its form should also be independent of the apparatus used.

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1) In other words independently of the concrete form of the required relation $S = S(J)$.
2) If the relation between the photoactivity of the X-rays and the wave length of the radiation is not considered.
3) If the symmetry of the $K_{\alpha_{1,2}}$ line is not destroyed.

In order to use the blackening curve constructed by the method described above it is convenient, however to transform it into a form which is independent of the selection of the values for the initial intensity – I_0. This can be accomplished, if instead of the curve $S = S(I)$ a curve is constructed of log I against the ratio of the blackening of an arbitrary point on the experimental profile of the K_{α_1} line to the blackening of the K_{α_2} line at a point corresponding to its maximum. Both these values are determined by taking into account the background of the spectrogram. A curve of this type which was obtained for a Mark XX plate is represented in the figure (upper portion). It was constructed on the basis of a large number of independent points obtained by the use of the $K_{\alpha_{1,2}}$ doublets of Cu and Zn, taken with a Johann-Koshu spectrograph.

By means of the curves given in the diagram it is possible to get highly accurate analyses within the range of ratios of S/S_r from 0.3 to 1.3. The amount of the element used for comparison in the sample ignited should be chosen (as shown experimentally) so that the blackening of the K_{α_2} line appears to lie within the limits 0.2 to 0.75. When this is done the deviation of the experimental points from the curve represented in the diagram is negligible. Outside the range for S/S_r given above, the extent of the agreement between the experimental values of J/J_0 and the values determined from the curve decreases and appears to be dependent on S_r.

On the lower part of the diagram graduation curves are represented which were obtained by means of two series of specially prepared synthetic mixtures, in which the content of the element to be determined was varied while the content of Zn (the element used for comparison) was kept constant at 20% and 40% respectively. Comparison of the upper and lower curves enables an analysis to be carried out with an accuracy of not less than 4-6% of the actual amount. This is done by measuring the blackening of the corresponding lines of the element to be analyzed and the blackening of the maximum of the K_{α_2} line of the comparison element. The results and accuracy of the analyses when this method is adopted are practically independent of the variation in exposure time and the working condition of the spectrograph tube, and also of the variations in the background of the spectrogram. There is no need for any special conditions for developing the spectrograms. At the same time, the fact that within the wide concentration range of the element to be analyzed in the test sample, the content of the comparison element can remain strictly constant, enables one automatically to take into account the change in the conditions for applying the substance to be analyzed to the surface of the anticathode of the X-ray tube, and to reduce to a minimum the detrimental effect of this factor on the accuracy of the analyses. Thus the comparison element used in our experiments also plays the part of a "fixing element" so that differences in the conditions used for excitation of the X-rays in test samples which cover the surface of the focussing spot of the X-ray tube differently, need not be taken into account.

In conclusion it can be stated that the method described above[1)] for constructing a blackening curve can be used for quantitative analyses and can be applied in X-ray structural analyses and in optical and other fields of investigation.

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1) After some minor modifications.

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A DISMOUNTABLE X-RAY TUBE WITH A REVERSE RAY PATH FOR X-RAY SPECTRAL ANALYSIS

I. D. Shevaleevsky

The Institute of Geochemistry and Analytical Chemistry, Academy of Sciences USSR, Moscow

Despite the numerous merits of the X-ray spectral method of analysis, as far as its sensitivity is concerned it cannot compete with optical methods in the majority of cases. One of the main factors which lowers the sensitivity of X-ray chemical analysis is the continuous spectrum; its presence on the spectrogram during analysis of samples containing small amounts of the element to be determined often makes it impossible to distinguish the lines of the characteristic spectrum on such a background. One of the methods therefore of increasing the sensitivity of the X-ray method is to weaken the continuous background as much as possible.

The most radical method of solving the problem, whereby, at least in theory the background of the spectrogram which is determined by the continuous spectrum can be almost completely eliminated, was that proposed in 1936 by Blokhin [1] and after 11 years "rediscovered" by Holubei and Cauchois [2]. This method is based on the fact that in contrast to the characteristic X-ray radiation which is propagated in all direction with equal intensity, the continuous spectrum which interferes in X-ray chemical analyses is polarized. It has, as many investigators have shown, a minimum intensity in the direction of the retardation of the cathode beam which excites the X-rays and amounts to not more than 15% of the intensity of the radiation, measured in a perpendiculer direction. Therefore if the X-rays are directed from the tube in the direction of impact of the cathode electrode beam, then theoretically it should be possible to separate almost completely the characteristic spectrum from the continuous one.

In spite of the undoubted merits of the idea mentioned above, hitherto not only has no reliable apparatus based on this idea been constructed or the idea accepted in practice by investigators in this field, but it has not even been reliably tested experimentally (as far as can be judged from literature sources). We are aware that the tube constructed by Blokhin is not irreproachable.

It seemed expedient therefore to construct an experimental model with a reverse ray path and to study its merits and demerits for carrying out X-ray chemical analyses (vide Fig. 1).

The tube is mounted on the base of an RSK-i X-ray spectrograph. The casing is a rectangular brass block with openings for anticathode, high vacuum pump and an LT-2 for measuring the vacuum and a slit for emmission of the X-rays. The anticathode was fixed on a porcelain insulator with four screw clamps. The insulator on the conical section fixes into the tube casing. The cathode is prepared in the form of a rectangular cover in which a slit is cut, covered with an aluminum foil 20 μ thick. The foil which separates the internal part of the tube from the atmosphere is clamped to the cathode by means of a special lamina fitted with a thin lead gasket. The cathode is clamped with four bolts fitted with rubber gaskets to the tube casing, while the filament with focussing flanges fixes into the slit of the tube casing. A straight platinum wire 0.3 mm in diameter and 45 mm long was covered with strontium oxide. By using conical sections and threaded

spindles on which the filament with focussing flanges is mounted, the distance from anticathode to filament can be changed under high vacuum from 15-35 mm. The tube operates at its optimum when the distance between cathode and anticathode is kept within the limits of 17-20 mm. The cathode and the tube casing were not cooled artificially, because although the tube was operated for 2 hours at 45 kV and 20 mA, the apparatus only heated up to 5-10° more than the surroundings.

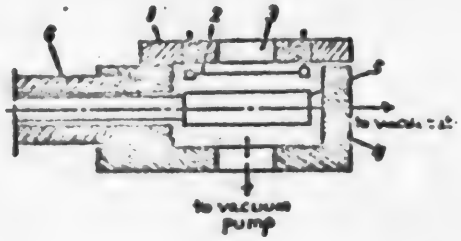

Fig. 1. Schematic features of the X-ray tube with reverse ray path. 1) cathode, 2) filament, 3) slit for the X-rays, 4) tube casing, 5) anticathode, 6) porcelain insulator.

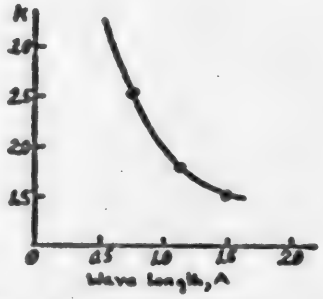

Fig. 2 Relation between the coefficient K and wave length.

After constructing the tube with a reverse ray path its performance was compared with that of a tube of normal construction. In order to do this, spectrograms were taken using an RSK-1 apparatus with the normal X-ray tube in addition to spectrograms taken with the new tube. The working ranges of both tubes were the same 45 kV at 20 mA. The exposure time was varied from 5-120 minutes. A quartz plate cut along the surface $(10\bar{1}0)$ and bent along a 100 cm radius was used as the reflecting surface. The value of the working part of the crystal was 4 mm in all cases. The focussing spot on both apparatuses was 20-24 mm long and 5-6 mm wide. The test mixture, prepared by chemical methods and containing oxides of Ta, Nb, As and Sn, was smeared on the rifled cathode surface. The radiation was registered by means of a two sided X-ray plate - XX (Russian make). Photometric measurements of the plate were made with a visual MF-2 photometer. The integral intensity of the lines was measured.

The $K_{\alpha_{1,2}}$ doublets of As and Nb for two orders of reflections were chosen as the supporting lines for the comparative study of the two X-ray tubes. The ratio of the blackening of the line of the characteristic spectrum to the blackening of the continuous background in the wave length range from 740 to 1490 Kh.E. that corresponds to Woolf-Bragg angles of 5-10°.

Average results for test runs of the two tubes are given in the table below. This table also includes values of the coefficient K, which characterizes the ratio of blackening of the comparison lines obtained with the two tubes to one value of the background.

Fig. 2 shows clearly that the tube with the reverse ray path is most effective in the short wave and low reflection angle region.

In spite of the limiting simplicity of construction of the experimental model described here with a reverse ray path and the snags associated with such a construction, its results are promising. We feel confident that the construction

of a more powerful and better constructed tube and the subsequent use of such an improved model in X-ray technique [3] should demonstrate the merits of this method for increasing the sensitivity of the X-ray method to greater advantage.

Element	Order of reflection	Si/Sf		K
		Normal tube	Tube with reverse ray path	
NbK_{α_1}	I	2.21	5.67	2.56
AsK_{α_1}	II	6.97	12.59	1.80
NbK_{α_1}	II	3.01	4.67	1.54

In conclusion I should like to express my thanks to E. E. Vainshtein for proposing this scheme of work and for his help in its fulfillment.

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NEW APPARATUS FOR ELECTROCHEMICAL METHODS OF ANALYSIS

V. A. Zarinsky

Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

A Streaming Mercury Cathode

Mercury cathodes in the form of a jet are used for preparative purposes in electrochemistry, for preparing metal amalgams [1] for the electro-reduction of organic compounds [2], for studying the mechanism of cation discharge [3] and in oscillographic polarography [4].

The set-up which we have constructed, which includes a streaming mercury cathode, is depicted in Fig. 1. Chemically pure mercury is contained on the bottoms of the three connected vessels 1,2 and 3.[1] 11 is connected via a tap 10 to 9; 9 can be evacuated by means of a water jet pump, connected to tube 5. Mercury from the

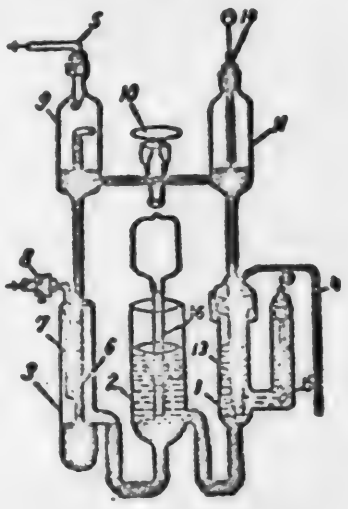

Fig. 1. Set up for streaming mercury cathode. 1) electrolyzer; 2) partition for decomposition of the amalgam; 3) mercury receiver; 6) tube for leading mercury into 9; 7) T-piece with valve 8 for leading in nitrogen; 5) connecting tube to water pump; 10) tap; 11) bulb for passing mercury to the electrolyzer; 13) capillary tube; 15) anode; 4) electrolytic switch for electrode comparison.

bottom of 3 rises in tube 6 up to the T-piece junction at 7. By the action of a stream of nitrogen, sucked through valve 8, the mercury column in tube 6 breaks up into separate parts and is sucked into 9. After filling 9 with sufficient mercury, the vacuum is switched off and tap 10 is opened; the mercury flows in 11 and from there along capillary tube 13 in a jet into 2 (the electrolyzer).

The set-up subsequently works automatically by switching on the vacuum. The amalgam formed by cathodic polarization of the mercury jet flows from 1 into 2, where it is decomposed by means of acid and is mechanically stirred with a glass stirrer 16. The mercury goes from 2 to 3, from which it again rises into 9, etc.

Thus in the apparatus described the same mercury is used over and over again for obtaining a continuous jet of mercury, which serves as a cathode for an indefinite time.

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[1] For methods of purifying mercury see [5].

The negative pole of the current supply source is connected to the platinum contact 14, while the platinum anode is fixed in the side tube 15. The potential of the streaming cathode is measured during polarization by reference to a saturated calomel electrode by the usual compensating system. The distance of the end of the electrolytic switch from the mercury surface is fixed because the switch and the capillary tube 13 are fused into the cover.

Fig. 2 Restriction of the lower end of the jet.

It was observed that with increasing current density the jet does not remain constant but increases. Under the action of the current the jet breaks up into small drops, the place at which the break up occurs however cannot be established even under strong magnification. In some essential cases (e.g. for calculating current density) the lower end of the jet can be confined with the help of a little shaft, fused into the cell wall (Fig.2)[1].

An Apparatus with a Renewable Flat Cathode

Of all the apparatuses described hitherto which have a renewable mercury cathode [5,8], the Hildebrand cell is the most often used in electroanalysis [9]. We found that during the electrolysis of weak solutions of metals which can form amalgams, this apparatus does not always ensure good results in the sense that the separation of the metal is complete and pure. This can be explained by a) an insufficiently intense exchange of mercury between the two separation cells, which leads to a change in the deposition potential of the metal as the result of an increase in its concentration in the amalgam located in the cathode compartment; b) the penetration of undecomposed electrolyte into the compartment used for the decomposition of the amalgam.

These drawbacks have been eliminated in the apparatus depicted in Fig. 3. The mercury is located at the bottom of the two vessels 1,2 which are doubly connected, 2 serves as the electrolyzer in which the mercury on the bottom serves as a cathode; the anode is separated from the catholyte by a porous diaphragm 5. When the stirrer 6 in the form of a corkscrew is rotated, the mercury in tube 7 is pumped up into 1, in which its level becomes higher than that in 2, so that there is a flow from 1 into 2 via 8. The renewal of the cathode surface in 2 is also assisted by stirrer 9 driven by the motor 12 by a pulley attachment. The length of the vertical parts of tubes 7 and 8 is sufficient to hinder the penetration of the electrolyte from 2 into 1, where the amalgam is decomposed. The decomposition velocity of the amalgam can be increased by anodic polarization from an independent D.C. supply (e.g. a dry 1.5-2 volt battery); a platinum-tin electrode immersed in the electrolyte in 1 serves as the cathode in this case.

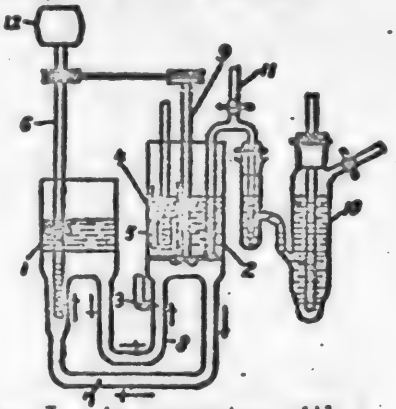

Fig. 3. An apparatus with a renewable flat cathode. 2) electrolyzer; 3) platinum contact; 4) anode; 5) porous diaphragm; 1) compartment for decomposition of amalgam; 6) corkscrew stirrer; 7-8) tubes for mercury flow and amalgam; 9) glass stirrer; 11) electrolytic switch; 10) standard electrode; 12-motor.

1) The streaming mercury cathode has the following advantages over a flat cathode a) the possibility of polarizing with a large current strength without appreciable heating of the solution as a result of Joule heating; b) lower concentration polarization because of the vigorous stirring of the solution by the mercury jet [7].

The cathode potential is standardized against an electrode suitable for any particular set of experimental conditions. A suitable form is shown in Fig. 3.

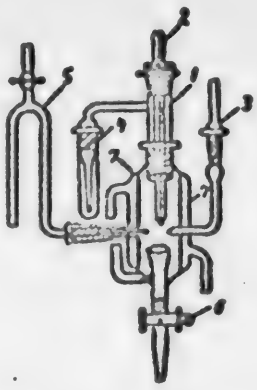

Fig. 4. Cell for polarographic analysis. 1) tube on a rod for strengthening the capillary electrode, 2,3,4) inlet and outlet tubes for hydrogen; 5) electrolytic switch; 6) outlet tap for mercury; 7) water jacket

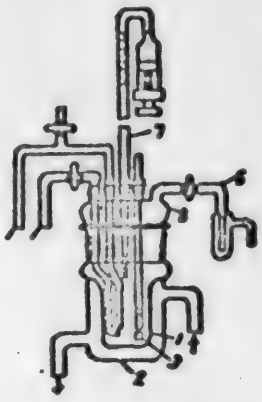

Fig. 5. Cell for potentiometric titration. 1) working volume (constricted part); 2) water jacket; 8) ground glass cover with tubes; 4,6 inlet and outlet tubes for nitrogen; 3) reference electrode; 5) electrolytic switch; 7) microburette.

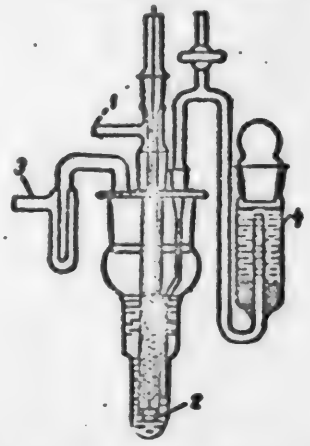

Fig. 6. A cell for pH determination by means of a hydrogen electrode. 1,3) inlet and outlet tubes for hydrogen; 2) platinum electrode; 4) saturated calomel electrode

Apparatus for Polarographic and Potentiometric Analysis 1 ...

a) A cell is shown in Fig. 4 which can be used for polarographic analyses with both external and internal anodes. In the latter case the potential of the mercury drop is measured by reference to a saturated calomel (or some other reference electrode) by means of the electrolytic switch 5. Capillary 2 is fixed on to a rubber cork, which is separated adequately from the solution in the cell. This separation is important in order to avoid contamination of the solution and deformation of the polarograph wave by the action of surface active materials [10]. The cell is thermostated by means of a jacket fused on to it, through which water heated to the required temperature in a Heppler thermostat is circulated.

b) Normally for potentiometric titration in an inert atmosphere all the details are mounted on the cork on a support [11]. Such a method is extremely inconvenient, particularly when working with very small volumes of solution, since it leads to accidents to some of the parts, and also to contamination from rubber connections, etc., when working with heated solutions, etc.

An apparatus is depicted in Fig. 5 in which all the details are mounted on a ground glass cover. 1-2 ml solution can be dealt with in the constricted lower part of the cell. In order to measure the potential accurately, two platinum electrodes are fixed into the cover, from the readings of which the average values are taken.

The apparatus is thermostated in the same way as described in apparatus (a).

c) When a pH is determined by means of a hydrogen electrode (Fig.6) there is no need to thermostat the apparatus since the temperature corrections can be calculated from a well known formula [12].

The author wishes to thank G. S. Tyurikov, P. N. Palei and I. A. Novikov for their help in constructing the apparatus.

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OBITUARY

VASILY IVANOVICH LISITSYN

(1886-1952)

Vasily Ivanovich Lisitsyn, an analytical chemist who was manager of the Chemico-Analytical Laboratory of the All Union Institute of Mineral Raw Materials and a director of the Geological Service, died on the 2nd of February after a long and grievous illness.

The Institute has lost a warm personality as well as an outstanding specialist in V. I. Lisitsyn, while the Chemical Society of the Union has lost a talented man who always helped those who turned to him for assistance.

V. I. Lisitsyn was born in 1886 of a peasant family. After completing a course at the Classical Gymnasium in 1903 he went to Moscow University.

He was arrested in 1906 for his revolutionary activities and sentenced to eight months in jail. In spite of this he finished his course in the natural physico-mathematical faculty of the University with honors; his outstanding capabilities were recognized by his Professor so that on graduating he was asked to remain at the University in N. D. Zelinsky's department. However the Trustees of the Moscow Scholastic circles refused his candidature because of his political unreliability.

V. I. Lisitsyn began his working life in various laboratories in Moscow, Leningrad and the provinces. Tuberculosis of the lungs, however, compelled him in 1918 to return to his native village where he led an agricultural artel until 1930.

When his health had improved, Lisitsyn entered the chemistry laboratory of the All Union Institute of Mineral Raw Materials (then the Institute of Applied Mineralogy) in 1930. After accepting the leadership of this laboratory in 1931, he remained there till his death.

In the course of his 22 years work at this Institute he showed superior capacities as a talented investigator and organizer.

The laboratory in his charge is rightly regarded as one of the best analytical laboratories in our country. In this laboratory the most important umpire analyses have been carried out. The laboratory fulfilled a large amount of work on the preparation of standard samples, and completed considerable research work, side by side with a vast amount of industrial analyses. In this laboratory, where Lisitsyn could combine both research and industrial collectives, more than 50 elements were determined.

Lisitsyn developed exceptional conditions for scientific research work, and for the training of scientific cadres. His co-workers in the laboratory published numerous papers in scientific literature and developed a large number of various analytical methods. Many of his co-workers completed and defended their theses, and several of them subsequently became doctors of science and professors.

In a review article devoted to the achievements of Soviet Science for the last 30 years, the laboratory led by Lisitsyn was numbered as one of the "outstanding schools of analytical chemistry in our country, a center of scientific

thought on analytical chemistry" (J. Appl. Chem. 20, 1045 (1947).

The most noteworthy characteristic of Lisitsyn's activity was his unceasing care for the development of laboratories of the peripheral geological administrations, and the training of cadres of young specialists in these laboratories.

Workers in the furthest laboratories of the geological administrations and on expeditions who turned to Lisitsyn always received the closest attention to all their questions, together with exhaustive consultations and comradely support. His faultless work over many years in the service of our Socialist country was highly valued by the Government. He received Government awards and thanks.

In V. I. Lisitsyn we have lost a warm personality, a talented analyst, and a considerate and skillful leader.

Everyone who met Lisitsyn while he was alive will cherish his memory.

Yu. S. Lyalikov. "Physico-Chemical Methods of Analyses" (A Textbook for Metallurgical Students and for Students of Coke Chemistry) 2nd edition, revised and enlarged. Met. Press. Moscow, 1951, 308 pp. with illustrations. 10 roubles 95 kopecks

The appearance of a 2nd edition of Lyalikov's textbook is proof of its merits and the need for this book, in which all the more or less widely known and often used physico-chemical methods of analyses are set out in an accessible form. Although the book is designed as a textbook for metallurgical and coke-chemistry technical schools, it can, for lack of a more fundamental textbook, serve as a hand book for workers in factory laboratories and for students in chemistry colleges.

Yu. S. Lyalikov, having taken into consideration all the observations and wishes regarding the 1st edition, has subjected his book to a fundamental revision which has enhanced its value considerably. It is particularly consoling to observe that in a new chapter the author has given a fairly detailed treatment of the part played by our country's scientists in the development of physico-chemical methods of analyses and has corrected historical errors in relation to the contribution of Russian and Soviet scientists in this field.

In this new edition, the chapter devoted to spectroscopic analyses has been left out without sufficient reason. If the aim of this textbook is to acquaint students with fundamental physico-chemical methods, then the author should either thoroughly correct and remodel the chapter indicated, or hand it over to a competent specialist. A reference to the effect that there are already in existence or that there are specialist textbooks in preparation on spectroscopy is unconvincing. Other chapters could be included with equal success. Meanwhile spectroscopy, as one of the most important and valuable physico-chemical methods of analyses, should find its rightful place in any textbook devoted to the field of analytical chemistry.

At the end of each of the eleven chapters, problems and questions are included which facilitate the utilization of the material set out.

General information and the principles of mathematical and graphical treatment of results of observation are set out in the 1st chapter. The description of the graphical treatment of results is somewhat shorter than in the 1st edition. This cannot be justified, because of its importance to students.

The second chapter is devoted to visual colorimetry. The material is set out exhaustively in a manner readily accessible to the beginner. Both theoretical and practical questions are treated well. The method of describing the apparatus, its use, and the selection of practical work is very successful. Unfortunately the author continues in this new edition to switch his terms in an arbitrary fashion; e.g. light strength, amount of light, intensity of light, light value, etc.

The theoretical basis and practice of nephelometric analysis is given in Chapter IV. There are no essential drawbacks. It is incomprehensible, however, how in § 2 in the description for converting the normal colorimeter into a nephelometer, it is possible to observe by means of an eye piece a light beam

scattered by particles, when the author recommends that the immerser be covered with a black lacquer. He probably means that only the side walls of the immerser should be covered and not the lower surface.

Chapter IV is devoted to a rather full discussion of the theoretical basis, the apparatus, and the technique of photocolorimetry in a way that indicates a good knowledge of the material.

There are a few inaccuracies and unclear formulations, e.g. on p. 273 it is stated that on applying a certain potential to two plates fixed in a vacuum, a current does not flow in the circuit because electrons do not traverse a vacuum, and further on illuminating the cathode, electrons break away which proceed to the anode and a current flows in the circuit. It is pertinent to speculate on the manner in which the electrons move in a vacuum in the 2nd instance, if as the author affirms earlier, they cannot traverse a vacuum. On p. 78 it is stated re the photoelement with an internal photoeffect: "if a certain potential difference is preliminarily applied to the electrode" while the author has in mind the application of the potential difference to the two electrodes. The application and selection of light filters is not successfully explained (pp 86-87). It would not be amiss to give a definition of lumen. Here again we meet with the parallel use by the author of the term intensity and strength of light for one and the same phenomenon. The mathematical relation between the voltage applied to the light source and the strength of the light flow is not completely accurately formulated on p. 90. This definition does not correspond fully with the graphical representation of this relation given there. On p. 100 in a description of the preparation of solutions for constructing a calibration curve, the author having dissolved 1 g of steel succeeds somehow or other in adding to one and the same solution 2, 5, 7.5... 25 ml of a standard solution of Ni, and prepares a series of solutions with different concentrations of Ni! There are also errors in answers to problems, e.g., p. 102, problem 2, etc.

In Chapter V the author deals with the refractometric method of analysis. The amount of information given corresponds to the practical importance of the method. The most widely used apparatus in laboratory practice has been picked out, together with theoretical information, and examples are given for practical work with the apparatus described.

The derivation of refractive index and the formulation of this concept is not clearly expounded. The author correctly defines the refractive index as the ratio of the sine of the incident angle to the angle of refraction for light passing from one medium into another. Further on however he states "When a ray of light passes from a more refracting medium into a vacuum or into air, for which the refractive index is equal to unity etc.", of course one medium on itsown cannot possess a refractive index. Similarly the refractive index in formula (2) cannot be deduced from equation (1) p. 105, when sine β is equal to unity. It is not indicated in Table 12 what media the refractive indices of the tabulated substances refer to.

The polarometric method is discussed in chapter VI. The principle of the method is briefly described, together with the fundamental apparatus and technique. Unfortunately on p. 125, where the equation relating the specific rotation of the plane of polarization is given, it is not clear whether the sign denotes a minus or a hyphen. On Fig. 86 the ratio between d_1 and d_n is wrongly expressed. On Fig. 89 the column 16 is not marked etc.

Electroanalysis is considered in chapter VII which is one of the most reliable ones. Although considerable space is devoted to electrolysis, the exposition is not always clear and systematic, and in some instances suffers from simplification, e.g. in the explanation of the origin of electrode potentials, chemical polarization, etc. One of the drawbacks of this chapter is

the discussion of all the theoretical bases of electrolysis in only 24 pages, in which are included discussion of normal electrolysis, internal electrolysis, overvoltage, polarization, and practical questions, without any indication of the relations between them. The way in which this chapter has been compiled hinders reading and use of the material.

Apparatus, technique and practical problems are described thoroughly. Errors noted here are as follows. The way in which the equation of the discharge of PbO_2^{2-} to give PbO_2 on p. 153 gives rise to doubts as to whether it is the ion $Pb^{4+}O^{2-}$ or the molecule PbO_2. There is no congruence between a statement in the textbook (p. 157) to the effect that in a neutral medium $E_{Ni} < E_{Cu}$ and $E_{Ni} > E_{Zn}$ and the results adduced in Table 19. On p. 171, § 4 as the first practical problem it is suggested that Cu and Sn can be determined by electrolysis, when in fact it should be Pb and Cu.

The student will find the necessary information in chapter VII for learning the principles of conductometric analysis. It is described concisely and clearly. The lamp methods described are not quite so accessible.

Potentiometric methods are the subject of chapter IX - it occupies most space in the book despite the fact that the basic question of the origin of electrode potentials has already been discussed in the chapter on electroanalysis. Here additional information is given on the development of the oxidation-reduction potential, without a discussion of the mechanism of the origin of these potentials. All the four types of reactions which are used in potentiometric analysis are considered. The theoretical and practical material presented in this chapter is fairly comprehensive. Different types of electrodes are described, together with experimental set ups and apparatus for titration. Unfortunately, the author has nothing to say about potentiometers, either lamp types or simple ones, as issued by the MOSKIP factory. This observation applies equally to photocolorimeters - mark FEK-M, MOSKIP, etc. Young students should be made aware of Russian apparatus which is available.

Chapter IX contains the greatest number of mistakes, misprints, innaccuracies and nebulous formulations, e.g. in the formula for potentials of systems, although factors which are responsible for deviations from normal potentials are indicated, the reasons for these deviations are not discussed. The derivation of the potential at the equivalence point is not well put. It is not at all clear what the author means by the initial concentrations of the reaction products. The stetement that the equilibrium potential of an oxidation-reduction system is defined as the average arithmetic oxidation-reduction potential of the system participating is incorrect. The choice of the term "antimony oxide electrode" is an unfortunate one, since it has been customary to use the term "antimony electrode" for a long time. On p. 212, in calculating the titration potentials of silver cyanide, the minus sign is continuously omitted. On p. 154, the level of the liquid in the hydrogen electrode is incorrect. In Table 28 it is correctly stated that the potential of the antimony electrode depends on the method of preparation; but for the glass electrode a mathematical relation is given between potential and hydrogen ion concentration. Maybe the potential of the glass electrode is a constant for all cases and is independent of the method of manufacture and the composition of the glass!! It is incomprehensible how a reverse titration of Co^{2+}, Ni^{2+}, Zn^{2+} (Table 29) can be carried out, by means of a silver electrode, with $AgNO_3$ as the working solution. In the graph of the exchange potentials, normal potentials of the systems are given; these concepts are heterodynamic. Further it is not clear how it is possible to titrate pentavalent vanadium with permanganate, cerium sulfate (IV) and chromium sulfate (II). Incidentally the ion V^{3+} does not exist. The same can be said about the impossibility of titrating

iodides, $Ce(SO_4)_2$-iodates, $CrSO_4$- bivalent Fe, etc., with $TiCl_3$. Such misprints are inadmissible in a textbook. A method for non-compensated titration up to the point when there is no current in the system, is incorrectly described, because nothing is said about the choice of suitable reference electrodes for each individual case.

In the section devoted to practical work, mistakes crop up again, e.g., it is not clear why, during potentiometric titration of iron with dichromate, it is essential to add phosphoric acid. The method described for the titration of iodides with silver ions leads to large errors because of the adsorption of iodine ions by the precipitate. The addition of barium nitrate is recommended in order to increase the accuracy and stability of the electrode potentials. The author's suggestion of platinizing platinum electrodes in the determination of the pH of a solution with the quinhydrone electrode is a dubious one. Incidentally platinization is not described correctly. After platinization, the electrode in sulfuric acid should be the cathode and not the anode as the author advises.

The best chapter is chapter 10 which is devoted to polarography. The author also considers amperometric titration, since it is based on the same principles. This chapter, with regard to its lay out and from both theoretical and practical aspects, is the most successful, and does not call for any comment save that it is a pity the rest of the book is not on such a high level.

In chapter XI the thermoelectric and luminescence methods are discussed, together with analyses based on determination of the surface tension of solutions. The exposition of the first and third methods is strictly schematic. The luminescence method is described in more detail. Students should be able to gain sufficient elementary information for practical application of the method

On the whole it may be said that Yu. S. Lyalikov's textbook is a very useful and valuable book which fills a serious gap in Russian textbooks. In making a first attempt at describing the most important physico-chemical methods of analysis in a textbook, the author naturally could not avoid making a number of mistakes in the theory and in its practical applications, but these can be easily corrected in future editions.

P. K. Agasyan.